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Aerosol Source Characterization Study in Miami, Florida. Microscopical Analysis

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Aerosol Source Characterization Study in Miami, Florida

Microscopical Analysis

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EPA-600/3-79-097
September 1979

AEROSOL SOURCE CHARACTERIZATION STUDY IN MIAMI, FLORIDA
Microscopical Analysis

by

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ABSTRACT

In June of 1975 the EPA conducted an experimental program in the Miami metropolitan area to collect atmospheric aerosol samples. The sample compositions were to be identified in order to determine the aerosol sources.

Several different sample types were taken for mass, elemental, and compound analyses. One group of samples was collected on substrates suitable for elemental analysis. Elemental analysis was conducted using the PIXE (proton-induced x-ray emission) technique (Johansson et al., 1972). A second group of samples was collected on substrates suitable for optical and scanning electron microscopy.

The microscopical analyses, conducted by IIT Research Institute, show the composition of Miami's TSP (total suspended particulate) to be very similar to that of Chicago, St. Louis, and Philadelphia, with the exception that Miami receives a significant impact from ocean spray. Mineral fragments resuspended by traffic appear to be the primary aerosol mass contributor. Rubber tire fragments and carbonaceous vehicle exhaust are also major TSP contributors. These conclusions are based solely on three sampling days at three sites and need to be confirmed by additional studies. However, it is very likely that the aerosol types and amounts reported above remain fairly constant throughout the year. The results of PIXE analyses done on the first group of samples are summarized in a separate report (Hardy, 1979).

This report was submitted in fulfillment of Grant No. R803078 by IIT Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 4, 1975, to June 12, 1975, and work was completed as of August 1977.

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Elemental concentration data, determined by Drs. Jack Winchester and William Nelson of Florida University, are used in this report and gratefully acknowledged.

SECTION 1

RECOMMENDATIONS

Following a review of the microscopical analyses, it was noted that an alternate method of analysis would have been feasible. The major compounds in the samples could have been identified quantitatively by means of microscopical petrography. Ammonium sulfate, calcite, quartz, carbonaceous particles, and the feldspars could have been analyzed sequentially as follows.

1. Determine the total projected area of all birefringent particles (measurement A). These would include ammonium sulfate, calcite, quartz, and feldspars.
2. Dissolve the ammonium sulfate in water and determine the projected area for the remaining birefringent particles (measurement B). The difference between measurement A and measurement B is the projected area of ammonium sulfate.
3. Dissolve the calcite in dilute acid and determine the remaining projected area (measurement C). The difference between measurement B and measurement C is the projected area of calcite. The remaining projected area of birefringent particles is due to quartz and the feldspars. (This method may also be used to determine the particle size distribution of the components.)
4. Determine the projected area for the opaque carbon compounds such as vehicle exhaust, rubber tire fragments, and oil soot. The rubber tire fragments and oil soot can be distinguished from vehicle exhaust carbon by particle size discrimination. The spherical oil soot and cigar-shaped rubber tire fragments can be distinguished by their shape factors.

This method of analysis could account for more than 80 percent of the total aerosol mass. Each step requires approximately 10 minutes plus elapsed time for dissolution or chemical reaction. These analyses could be performed on glass fiber filters but ideally should be done on transparent, isotropic membrane filters. The Nuclepore Corporation of Pleasanton, California, has developed pilot batches of a transparent, isotropic, polycarbonate filter which could be ideal for this task.

SECTION 2

SAMPLING PROCEDURES

Aerosol samples were collected in Miami, Florida, between June 4, and 12, 1975. Three sampling sites were selected and designated M-10, M-11, and M-14. Site M-10, 6400 N.W. 27th Ave., was a U.S. Marine Corps Station. Site M-11, 251 E 47th St., was located at Hialeah High School. Site M-14 was a fire station at 6000 S.W. 87th Ave.

Hi-vol samplers and eight-stage Andersen impactor samplers were used to collect aerosol samples at the three sites. The aerosol cut-off size, D_{50} , for each impactor stage is shown in Table 1. Samples for microscopical analysis were collected on June 4, 11, and 12. The original sampling protocol called for the use of Millipore membrane filters on Stages 0-4 and Nuclepore membrane filters on Stages 5-7 of the impactor samples. Millipore filters were to be used as backups. Inadvertently, Millipore filters were used for all eight stages during the first day of sampling (June 4), and Nuclepore poreless filters were used for all eight stages during the remaining two days of sampling (June 11 and 12).

Nuclepore filters are birefringent and thus interfere with polarized light microscopical studies of particles. Therefore, detailed optical microscopic studies could be made on the June 4 samples only. Table 2 lists the samples submitted for microscopical analysis.

SAMPLE PREPARATION FOR OPTICAL AND SCANNING ELECTRON MICROSCOPY

Hi-vol Sample Preparation

Wedge-shaped sections were cut from each filter and placed on glass slides. They were then immersed in a liquid with a refractive index of 1.515. The liquid

matched the refractive index of the glass fibers, rendering them invisible during the ensuing examination by optical microscopy.

Andersen Impactor Sample Preparation

Sections of 10 mm by 35 mm were cut from the Millipore filter substrates and immersed in 1.515 refractive index liquid on glass slides. Deposits on the Nuclepore filters were examined dry on the uncut filters by both transmitted and reflected light.

Scanning Electron Microscopy--

Small sections of selected filters from the impactor samples were mounted on carbon stubs for scanning electron microscopy (SEM) and x-ray fluorescence analysis. Samples collected on both Millipore and Nuclepore membrane filter substrates were analyzed by these two methods. The hi-vol filter samples were analyzed by optical microscopy only.

SECTION 3

MICROSCOPICAL SAMPLE ANALYSIS

ANALYSIS OF SAMPLES COLLECTED JUNE 4, 1975

The glass fiber hi-vol filters were used to semi-quantitatively estimate the concentrations of specific aerosols. The estimates, based on percentages of total mass, are shown in Table 3. Although glass fiber filters are not ideal for optical polarized light microscopy, it is important to use a total sample to correctly determine the ratio of aerosol types present.

The Andersen impactor samples were submitted to both SEM and optical microscopy. The impactor samplers were especially important to this study, since they provided the key to the impact from ocean spray. From the many aerosol samples examined by the authors, the impactor samples were the only ones to show that calcium carbonate can form from water droplets containing calcium ions. This observation would not have been possible without the availability of the impactor samples.

Site M-10 Samples

Hi-vol Sample--

The sample consisted primarily of calcium carbonate particles in both a natural and recrystallized form (Figure 1). A few large, freshly cleaved quartz particles were present. Numerous large rubber tire particles and a great number of fine carbonaceous particles from automobile emissions were also contained in the sample. Oil soot and carbonized flakes from an incinerator type combustion source were trace sample components. Large sheets of decaying vegetation were a minor sample component. Definite sea salt crystals (Na, K, and chlorides) were detected but represented a very minor sample component.

Automobile traffic was the primary source for suspended mineral particles, as is evidenced by the large number and sizes of rubber tire particles. Ocean salt spray was also probably a major source of the TSP. However, it was extremely difficult to ascertain exactly what proportion of the collected particles was due to the ocean salt spray, because the calcium carbonate particles were generated by both automobile traffic and salt spray.

Andersen Impactor Sample--

Stages 0, 1, 2, and 3 each contained more mass than the comparable stages at Sites M-11 and M-14. The presence of many particles larger than the impactor stage cut size (Figure 2) indicates that a higher percentage of the sample consisted of recrystallized calcium carbonate. To prove that the recrystallized material present on Stage 4 was calcium carbonate, a filter segment was treated with dilute hydrochloric acid. Bubbles formed in the sample, indicating the evolution of CO_2 . After drying, most of the birefringent material (calcium carbonate) was absent (Figures 3 and 4). Stages 5 through 7 were similar in composition to the M-11 and M-14 impactor samples. However, the higher mass loadings on the M-10 sample permitted the growth of several very large ammonium sulfate crystals on Stage 7 (Figure 5).

Scanning Electron Microscopy--

- Stage 0--An x-ray area scan of the entire particle deposit revealed calcium as the only peak distinguishable over background noise. X-ray analyses of individual particles confirmed the presence of rubber tire dust, quartz, feldspar, and iron oxide particles. Morphology indicated that many of the calcium containing particles were recrystallized on the filter surface from liquid (Figure 6). X-ray analyses of these particles confirmed they were calcium carbonate, since calcium was the only element present in the x-ray analyses.
- Stage 3--Calcium again was the primary element detected on an area x-ray scan of the particle deposit. However, distinct peaks for sulfur and chlorine (30 to 50 percent lower than calcium) were also noted above the background. X-ray analyses of discrete particles revealed the presence of calcium carbonate, calcium sulfate, calcium chloride, mixed calcium chloride-sulfate, potassium calcium phosphate, magnesium chloride, quartz, and feldspar particle types (Figures 7 and 8).

- Stage 5--An area scan of the deposition site revealed the presence of magnesium, aluminum, silicon, sulfur, potassium, calcium, and iron (Figures 9 and 10). Many large, cubical particles were found. Compositions varied from calcium carbonate to calcium chloride-sulfate, depending on the amount of matrix material surrounding the cubes (Figures 11-14). Particles toward the center of the impactor spot tended to be the calcium chlorides and carbonates. More sulfate species were present on the edges of the deposition. None of the very large recrystallized masses seen by optical microscopy were present in the deposits examined by SEM.
- Stage 7--The very large, flat, rectangular crystals seen by optical microscopy were present in the deposits examined by SEM. They were primarily ammonium sulfate with a trace of potassium (Figures 15-17).
- Back-up--Sulfur was the only peak distinguishable over the background in an area x-ray scan of the sample. Discrete particles containing various combinations of lead, bromine, chlorine, iron, and calcium were also detected by fixed spot analysis.

Site M-11 Samples

Hi-vol Sample--

Although calcium carbonate again was the primary particle type present, the concentrations of quartz, rubber tire dust, and fine carbonaceous particles appearing on the M-11 sample (Figure 18) were higher than those present on the M-10 sample. Recrystallized ammonium sulfate particles were also present in slightly higher concentrations compared to the M-10 samples. Other particle types exhibited comparable concentrations. Overall particle size was smaller on the M-11 sample, which probably accounted for the lower mass loading.

Automobile traffic was the primary generator of particles found on the sample. The auto influence was much stronger on this sample than on the M-10 sample. Ocean spray salt was present, but its contribution to total sample mass was difficult to assess.

Andersen Impactor Sample--

Stage 0 contained more large rubber tire particles and less recrystallized calcium carbonate (Figure 19) than did Stage 0 at Site M-14. This observation

was expected, since Site M-11 showed the highest automobile traffic influence on the hi-vol samples.

Stages 1 and 2 contained progressively more material, with higher percentages of calcium carbonate and lower percentages of rubber tire dust. Stage 3 was similar to Stage 3 at M-14 in that large prisms and dendrites of calcium carbonate had begun to appear (Figure 20). As on the M-14 sample, Stages 4 and 5 contained extremely large masses of recrystallized calcium carbonate (Figures 21 and 22). Ammonium sulfate crystals began to appear on Stage 5.

Stage 6 contained significantly more sulfate (Figure 23) than did the M-14 sample at Stage 6. Tailpipe emissions were the other major particle type present. Each deposition site (on Stage 7) contained very large crystals of ammonium sulfate along with many carbonaceous particles (Figures 24 and 25).

Site M-14 Samples

Hi-vol Sample--

This sample was closer in composition to the M-10 sample than to the M-11 sample. Calcium carbonate was the primary particle type present (Figures 26 and 27). Automobile related particles were also a major component. Recrystallized ammonium sulfate particles were present in slightly higher concentrations on this sample than on the M-10 sample.

As with the samples from the other two sites, automobile traffic was the major source for the collected particles. Again, however, ocean spray salt may have been a significant contributor to the TSP levels.

Andersen Impactor Sample--

Stage 0 was composed primarily of calcium carbonate, both natural and recrystallized. Rubber tire dust was present in large amounts (Figure 28). A minor amount of quartz was also present. Approximately 30 percent of the calcium carbonate present was recrystallized from liquid droplets (Figure 29). Modal size for particles on this stage was 10 μ m.

Stage 1 was similar in composition to Stage 0. However, a higher percentage of the calcium carbonate was recrystallized compared to the Stage 0 sample. Modal particle size was approximately 8 μm (Figure 30).

Stage 2 contained significantly more particles than the first two samples. Calcium carbonate remained the primary sample component, and significant amounts of rubber tire dust were also still present (Figure 31). Oil soot was also present on this stage. The concentrations of glassy fly ash and biological particles were higher than those on the previous two stages. Modal particle size was approximately 5 μm (Figure 32).

More material appeared on Stage 3 than on Stage 2. Calcium carbonate was present in higher concentrations than on the previous stages, and very large recrystallized calcium carbonate particles had begun to appear (Figure 33). That these particles were recrystallized is evidenced by their very large size compared to the rest of the particles (Figure 34). Rubber tire dust decreased in concentration, and clumps of fine carbonaceous tailpipe particles appeared.

Stage 4 contained huge crystals of regrown calcium carbonate. The recrystallized material comprised at least 6 percent of the mass on the stage (Figures 35 and 36). The concentration of carbonaceous particles primarily derived from tailpipe emissions increased. Modal particle size, as indicated by the fly ash spheres, was approximately 2 μm (Figure 37).

One large recrystallized calcium carbonate mass composed most of Stage 5 (Figure 38). Carbonaceous auto exhaust particles were the second most abundant particle type present (Figure 39). A second type of recrystallized particle began to appear on this stage, and small ammonium sulfate crystals were present.

Carbonaceous (tailpipe) particles were the major components of Stage 6 (Figure 40). Small amounts of recrystallized ammonium sulfate particles were also present (Figure 41).

Stage 7 was composed primarily of large thin sheets of recrystallized ammonium sulfate (Figure 42). Tailpipe emissions were the second most abundant particle type by mass.

The back-up filters contained carbonaceous particles and a few fine mineral particles only.

ANALYSIS OF SAMPLES COLLECTED JUNE 11, 1975

Site M-10 Samples

Hi-vol Sample--

The sample was composed primarily of calcium carbonate. In comparison to the June 4 sample a higher percentage of the carbonate in this sample was recrystallized from liquid droplets (Figure 43). Although automobile related particles were lower in concentration compared to the June 4 sample, automobile traffic was still the primary source for particles found in the sample. The major difference between the June 4 and June 11 samples was the presence of great numbers of small ($1\text{ }\mu\text{m}$ - $3\text{ }\mu\text{m}$), highly birefringent, spherical particles on the June 11 samples. These spheres were recrystallized particles of ammonium sulfate, calcium carbonate, and calcium sulfate. Their presence indicated a significant ocean spray salt contribution to the TSP level on this date.

Andersen Impactor Sample--

Each stage of the M-10 sample contained more mass than comparable stages at Sites M-11 and M-14. M-11 and M-14 samples were relatively similar in composition; M-10 samples differed slightly from these.

Stages 0-3 were composed primarily of recrystallized salt particles. Stage 1 showed a lower percentage of recrystallized material compared to the same stage of the M-11 and M-14 samples. Stage 4 contained very large recrystallized calcium carbonate masses. Stages 5 and 6 were so heavily loaded with material that it was impossible to determine particle morphologies. The Stage 7 deposits consisted of several huge ammonium sulfate crystals forming a ring around a carbonaceous particle center.

Scanning Electron Microscopy--

- Stage 0--Many well-formed, recrystallized particles were found on this stage (Figure 44). Calcium was the primary element present. It occurred in carbonate, sulfate, and chloride forms; it also appeared in mixed particles with chlorine and potassium, or chlorine and sulfur. Discrete particles of sodium chloride and magnesium chloride were also present.
- Stage 4--Particles on this stage were frequently discrete particles deposited as solids (Figures 45-47) rather than liquids, compared to this stage on June 4. X-ray scans of the entire deposition site indicated silicon was the major sample component (Figure 48). The composition of the deposit varied considerably from the center to the edges.
- Stage 7--A deposition site composed of a dark, carbonaceous center mass surrounded by large crystals (10 to 30 μ m ammonium sulfate) was analyzed by SEM (Figure 49). The large crystals showed only sulfur when x-rayed (Figure 50). Large, snowball-like clusters in the center of the deposition were primarily ammonium sulfate; trace quantities of sodium were detected in these particles (Figure 51). The center of the deposition area contained primarily sulfur, with silicon, aluminum, potassium, calcium, and iron (listed in order of decreasing abundance) also present (Figures 52 and 53).

Site M-11 Samples

Hi-vol Sample--

As on June 4, automobile related particles were higher in concentration on the M-11 sample than on the M-10 and M-14 samples (Figure 54). The sample was quite similar in composition to the June 4, M-11 sample. Calcium carbonate was the primary particle type present. The fine, spherical, highly birefringent particles seen on the June 11, M-10 sample were also present in large numbers on the M-11 sample (Figure 55). Ocean salt spray contributed approximately 30 percent of the sample mass.

Andersen Impactor Sample--

Stages 0 through 3 each contained more total mass than did the comparable M-14 samples for this date. Recrystallized rhombs and dendrites of calcium carbonate, sodium chloride, potassium chloride, and calcium chloride contained the majority of the sample mass on these stages. Rubber tire dust was also a

major component on Stages 0-3. Stage 4 contained a very large recrystallized calcium carbonate mass similar to the one seen on Stages 4 and 5 of the M-14 sample. Particles on Stages 5 and 6 were piled heavily on top of each other, precluding the determination of particle morphology. Stage 7 contained huge ammonium sulfate crystals in the center of the main deposition site. Carbonaceous particles were major components of Stages 4 through 7.

Scanning Electron Microscopy--

- Stage 0--Calcium was the primary element present. A lower percentage of the recrystallized calcite particles was present compared to the M-10 sample. A larger amount of magnesium, sodium, and potassium, chlorides and sulfates was present on this stage at Site M-11 than on Stage 0 for the June 11, M-10 sample.
- Stage 3--Silicon, aluminum, chlorine, sulfur, and calcium were the primary elements found in the recrystallized particle mass (Figures 56 and 57). Many well formed sodium chloride cubes were present (Figure 58).
- Stage 7--Sulfur was the primary element detected in an x-ray scan of the total deposition; very small amounts of silicon, aluminum, potassium, calcium, sodium, iron, lead, and bromine were also detectable over the background. The major recrystallized species present was ammonium sulfate (Figure 59).

Site M-14 Samples

Hi-vol Sample--

Ocean salt spray was present in the heaviest concentration on this sample, representing 30 to 40 percent of the sample mass (Figure 60). Automobile related particles, including rubber tire dust, tailpipe emissions, and roadway pavement, were major sample components. Calcium carbonate was the primary particle type. As on the other two samples for this date, large numbers of small, highly birefringent, spherical calcite particles were present (Figure 61).

Andersen Impactor Sample--

All stages were composed primarily of recrystallized particles. On Stages 0 through 3, the recrystallized particles were discrete rhombs and dendrites of

calcium carbonate, sodium chloride, potassium chloride, and calcium chloride. As did the Millipore filter samples, the Nuclepore samples on Stages 4 and 5 contained massive crystals of calcium carbonates. The samples on Stages 6 and 7 were very similar to the M-14 samples for June 4. A few very small sulfate crystals were present on Stage 6, whereas Stage 7 contained thin, flat sheets of recrystallized ammonium sulfate. Carbonaceous particles were the primary sample components on Stages 6 and 7 and major sample components on Stages 4 and 5.

Scanning Electron Microscopy--

- Stage 0--Recrystallized calcium carbonate, sodium chloride, and calcium chloride were the major particle types found on this stage (Figure 62).
- Stage 3--This sample was very similar in composition to the Stage 3, M-11 sample of June 11 (Figure 63). However, more of the particles were either recrystallized or cemented together by a sheet of recrystallized material (Figure 64).
- Stage 7--As with other Stage 7 samples, sulfur was the only element detectable over the background. The particle deposit was a thin sheet of ammonium sulfate, which encapsulated fine carbonaceous and mineral particles (Figure 65). Lead was undoubtedly present in the fine carbonaceous auto exhaust particles but was not detected with an area x-ray emission scan.

ANALYSIS OF SAMPLES COLLECTED JUNE 12, 1975

Brief examinations of the various time period samples from June 12 indicated only minor differences between these samples and those collected on the other dates. The M-10 sample showed the heaviest particle loading on all stages. Recrystallized salt particle concentration increased from Stage 0 to Stage 5. Because of shorter sampling time periods and therefore fewer particles, the massive calcium carbonate sheets were present on the Stage 5 samples only. As on the other sampling days, the Stage 7 samples from all three sites primarily contained large recrystallized ammonium sulfate sheets and particles, and fine carbonaceous (tailpipe) particles.

SECTION 4

COMPARISON OF MICROSCOPICAL AND ELEMENTAL DATA

Aerosol samples for proton induced x-ray emission analysis were collected simultaneously with the hi-vol and impactor samples at each of the three sites. These samples were collected in 2-hour sequential periods from midnight to midnight of each sampling day.

The elemental data from each of these 2-hour samples were averaged for the 24-hour sampling period to compare these results (Table 4) to the microscopy results. Each element was converted to its most probable compound or combining form (Table 5). These conversions are not exact since major elements such as calcium, sulfur, and silicon occur in several different compounds. However, the conversions are probably very close to the correct mass concentration for the samples, because the elements were converted to their most abundant compound or combining form in the samples. As a final step, to permit comparisons, the percentage of each compound in the sample was calculated (Table 6).

X-ray emission analysis showed that the total percentage of elements in compound form ranged from 7.4 to 47.7 percent. This calculation left an unaccounted balance ranging from 92.6 to 52.3 percent. Approximately 30 to 40 percent of this unaccounted balance was traceable to organics such as rubber tire fragments, carbonaceous auto and truck exhausts, and biological plant tissue. However, organics did not account for all the missing percentages. In fact, as the TSP mass concentration increased, the elemental concentration decreased. This inconsistency may have been caused by a large particle sampling bias, because the samples with higher mass concentrations were composed primarily of particles larger than 10 μm . Even if these large particles had been sampled proportionately, they probably would have yielded lower elemental concentrations resulting from x-ray self absorption effects. A decrease in

elemental concentrations also could have occurred for smaller particles, which tend to dissolve and recrystallize into large particles (such as was seen in each of the samples analyzed microscopically).

In spite of these differences, the elemental data showed a semi-quantitative trend in agreement with the microscopy results. Calcium (as calcite and feldspars) was the major component in each of the samples. Silicon and aluminum were also major elements. Silicon occurred in quartz and with aluminum as clays and feldspars. Sulfur was present principally as ammonium sulfate, then as calcium sulfate (gypsum). It also appeared in the rubber tire fragments.

Chlorine was present mainly as halite but also was found with calcium and magnesium as simple salts. The remaining elements were trace components of the samples, perhaps with the exception of phosphorous. Phosphorous was not detected in any of the mineral particles and was attributed to biological plant material, where it is usually found. Vanadium was detected exclusively in the oil soot particles. Titanium was found in some of the recrystallized salt particles but usually was present in glassy fly ash spheres from coal combustion and, of course in clay minerals. The titanium in these samples undoubtedly derived from clays encapsulated during crystallization of some of the salt particles.

We did not calculate the mass contribution from iron, manganese, nickel, chromium, strontium, and bromine, since it accounted for less than $2 \mu\text{g}/\text{m}^3$ in each 24-hour sample.

SECTION 5

RESULTS

The results of this study show automobile traffic and ocean spray were the primary sources of atmospheric aerosol in the Miami metropolitan area. Surprisingly, resuspended mineral particles from roadway surfaces rather than direct emission particles (i.e., rubber tire dust and tailpipe emissions) were the major contributors of automobile traffic. Recrystallized particles of sodium, magnesium, potassium, calcium, titanium, and carbonates, chlorides and sulfates were contributed by the ocean spray. These particle types were present in the air both as liquids and as dried solids. Since the ammonium sulfate forms appeared primarily on the smaller particle stages of the Andersen impactor samples, this compound more likely emanated from fossil fuel of automobiles and power plants than from ocean spray.

Sample compositions were very similar at the three sites; however, the degree of impact from the two sources varied. Site M-11 showed the greatest influence from automobile traffic, as was indicated by the large sizes and amounts of rubber tire dust present. Sites M-11 and M-14 exhibited a greater effect from ocean spray than did Site M-10.

The effect of the ocean spray was greater on the June 11 samples with the resultant wind direction from 100° than on the June 4 samples, when the resultant wind was from 340°. In fact, the increased TSP loadings on the June 11 samples appeared to be caused primarily by ocean spray.

The Andersen impactor samples provided invaluable information about the sources of the Miami atmospheric aerosol. Although the hi-vol samples contained large numbers of calcium carbonate particles, it was recognizable only on the impactor samples that at least 20 percent of the calcium carbonate

particles present were crystallized from liquid droplets. Since calcium carbonate is essentially insoluble in water, the calcite must have formed on the impactor stages. This hypothesis is corroborated by the observation that these crystallized calcite particles have a particle size which is 10 times greater than the D_{50} cut size of the impactor stage on which they formed.

The logical source of the droplets providing calcium ions is ocean spray. However, the samples did not contain the same ratio of sodium and magnesium to calcium as found in ocean water (26 and 3 respectively). This discrepancy suggests that some of the spray droplets may have been from fresh water sources.

Approximately 70 percent by mass of the atmospheric aerosol in Miami is below 3 μm in size.

TABLE 1. IMPACTOR CUT SIZE, D_{50}

Stage	D_{50} , μm [*]
0	16.4
1	9.3
2	5.35
3	2.95
4	1.53
5	0.95
6	0.54
7	0.38
8	back-up filter [†]

^{*} D_{50} values for Stages 2 through 6 determined by Flesch, et al., other D_{50} values are calculated.

[†] The backup filter was a 0.8 μm pore size, cellulose triacetate membrane (Millipore) filter.

TABLE 2. SAMPLES RECEIVED FOR ANALYSIS

Date	Sampling Period, Hours	Site	Sampler Type	Stages	Sample Numbers	Substrate Type
6/4/75	0000-2351	M-10	Impactor	0-7	011-018	Millipore
6/4/75	0000-2351	M-10	Impactor	Backup	019	Millipore-1*
6/4/75	0000-2351	M-10	Impactor	Backup	020	Millipore-2†
6/4/75	0000-2341	M-10	Hi-vol	TSP	00563	Glass Fiber
6/4/75	0002-2346	M-11	Impactor	0-7	020-027	Millipore
6/4/75	0002-2346	M-11	Impactor	Backup	028	Millipore 1
6/4/75	0001-2359	M-11	Hi-vol	TSP	00564	Glass Fiber
6/4/75	0047-2350	M-14	Impactor	0-7	021-028	Millipore
6/4/75	0047-2350	M-14	Impactor	Backup	029	Millipore-1
6/4/75	0047-2350	M-14	Impactor	Backup	030	Millipore-2
6/4/75	0010-2345	M-14	Hi-vol	TSP	00562	Glass Fiber
6/11/75	0004-2400	M-10	Impactor	0-7	071-078	Nuclepore
8/11/75	0004-2400	M-10	Impactor	Backup	079	Millipore-1
6/11/75	0000-2330	M-10	Hi-vol	TSP	00621	Glass Fiber
6/11/75	0014-2347	M-11	Impactor	0-7	074-081	Nuclepore
6/11/75	0014-2347	M-11	Impactor	Backup	082	Millipore-1
6/11/75	0003-2400	M-11	Hi-vol	TSP	00620	Glass Fiber
6/11-12/75	0125-0145	M-14	Impactor	0-7	091-098	Nuclepore
6/11-12/75	0125-0145	M-14	Impactor	Backup	099	Millipore-1
6/11-12/75	0125-0145	M-14	Impactor	Backup	100	Nuclepore-2
6/11/75	0102-2537	M-14	Hi-vol	TSP	00619	Glass Fiber
6/12/75	0000-0600	M-10	Impactor	0-7	PO-P7†	Nuclepore
6/12/75	0000-0600	M-10	Impactor	Backup	P8	Millipore-1
6/12/75	1345-1545 [§]	M-10	Impactor	0-7	P1-P8	Nuclepore
6/12/75	1345-1545	M-10	Impactor	Backup	P9	Millipore-1
6/12/75	0000-2348	M-11	Impactor	0-7	083-090	Nuclepore

TABLE 2. SAMPLES RECEIVED FOR ANALYSIS (continued)

Date	Sampling Period, Hours	Site	Sampler Type	Stages	Sample Numbers	Substrate Type
6/12/75	0000-2348	M-11	Impactor	Backup	091	Millipore-1
6/12/75	0230-0600	M-14	Impactor	0-7	101-108	Nuclepore
6/12/75	0230-0600	M-14	Impactor	Backup	109	Millipore-1
6/12/75	1300-1530 [§]	M-14	Impactor	0-7	111-118	Nuclepore
6/12/75	1300-1530	M-14	Impactor	Backup	119	Millipore-1
6/12/75	1605-2000	M-14	Impactor	0-7	120-127	Nuclepore
6/12/75	1605-2000	M-14	Impactor	Backup	128	Millipore-1

* 1 = 47 mm diameter

† 2 = 37 mm diameter

Inversion

[§] PO-P1, P8, P1-P8, and P9 were special runs involving TSI model 3100 Electrostatic Precipitator.

TABLE 3. COMPOSITION ON HI-VOL SAMPLES*

Aerosol Components	Site M-10		Site M-11		Site M-14	
	June 4 52.9†	June 11 84.0	June 4 40.5	June 11 66.4	June 4 31.1	June 11 44.3
Quartz	m	m	m-M	m-M	m	m
Calcium carbonate	P	P	P	P	P	P
Other minerals	m	M	m	m-M	m	M
Hematite	m	m	m	m-M	m	m
Magnetite	t	t	t	t	t	t
Rubber tire	M	M	M	M	M	M
Fine carbonaceous	m	m	m-M	m-M	m	m
Combustion-flyash	t-m	t	t	t	t	t
Decaying vegetation	m	m	m	m	m	t
Other biologicals	t	t	t	t	t	t
Ammonium sulfates	t	m	t-m	m	t-m	m
Sea salt	m	M	m	M	m	M
Oil soot	t	t	t	t	x	t

*P = Primary components, > 25% by mass; M = Major component, 5% - 25% by mass; m = Minor component, 0.5% by mass; t = Trace component, < 0.5% by mass.

†Total suspended particulate ($\mu\text{g}/\text{m}^3$)

TABLE 4. ELEMENTAL CONCENTRATIONS, $\mu\text{g}/\text{m}^3$

Date	Site	TSP	Element												
			Al	Si	P	S	Cl	K	Ca	Ti	V	Cu	Zn	Pb	Totals
6/04/1975	M-10	52.9	0.08	0.27	0.23	0.26	0.13	0.02	1.23	0.001	0.02	0.007	0.009	0.29	2.55
	M-11	40.5	0.03	0.22	0.20	0.16	0.10	0.004	0.31	0.001	0.07	0.021	0.003	0.23	1.35
	M-14	31.1	1.49	1.45	0.68	0.60	0.32	0.05	1.44	0.012	0.15	0.006	0.010	0.33	6.54
6/11/1975	M-10	84.0	0.30	2.66	0.67	1.13	1.85	0.36	4.76	0.113	0.03	0.002	0.024	1.6	13.50
	M-11	66.4	0.09	0.56	0.18	0.26	0.18	0.07	0.68	0.008	0.01	0.020	0.008	0.3	2.38
	M-14	44.3	0.14	0.84	0.22	0.37	0.70	0.14	0.94	0.035	0.01	0.005	0.006	0.2	3.61

TABLE 5. COMPOUND CONCENTRATIONS, $\mu\text{g}/\text{m}^3$

Date	Site	Al_2O_3	SiO_2	P_2O_5	$(\text{NH}_4)_2\text{SO}_4$	NaCl	K_2O	CaCO_3	TiO_2	V_2O_5	CuO	ZnO	PbO_2	Totals
6/04/1975	10	0.151	0.578	0.527	1.072	0.214	0.024	3.072	0.002	0.036	0.009	0.011	0.335	6.031
	11	0.057	0.471	0.458	0.659	0.165	0.005	0.774	0.002	0.125	0.026	0.004	0.266	3.012
	14	2.815	3.102	1.558	2.473	0.528	0.060	3.596	0.020	0.268	0.008	0.012	0.381	14.821
6/11/1975	10	0.567	5.690	1.535	4.657	3.050	0.434	11.887	0.188	0.054	0.003	0.030	1.847	29.94
	11	0.170	1.198	0.412	1.072	0.297	0.084	1.698	0.030	0.018	0.025	0.010	0.346	5.36
	14	0.265	1.797	0.504	1.525	1.154	0.169	2.347	0.058	0.018	0.006	0.007	0.231	8.08

TABLE 6. PERCENTAGE OF TSP BY COMPOUND

Date	Site	Al ₂ O ₃	SiO ₂	P ₂ O ₅	(NH ₄) ₂ SO ₄	NaCl	K ₂ O	CaCO ₃	TiO ₂	V ₂ O ₅	CuO	ZnO	PbO ₂	Totals	Unaccounted Balance
6/04/1975	10	0.3	1.1	1.0	2.0	0.4	0.04	5.8	0.004	0.1	0.02	0.01	0.6	11.4%	88.6
	11	0.1	1.2	1.1	1.6	0.4	0.01	1.9	0.004	0.3	0.1	0.01	0.7	7.4%	92.6
	14	9.1	10.0	5.0	8.0	1.7	0.2	11.6	0.1	0.9	0.03	0.04	1.2	47.7%	52.3
	10	0.7	6.8	1.8	5.5	3.6	0.5	14.2	0.2	0.1	0.004	0.04	2.2	35.6%	64.4
6/11/1975	11	0.3	1.8	0.6	1.6	0.4	0.1	2.6	0.04	0.03	0.04	0.02	0.5	8.1%	91.9
	14	0.6	4.1	1.1	3.4	2.6	0.4	5.3	0.1	0.04	0.01	0.02	0.5	18.2%	81.8

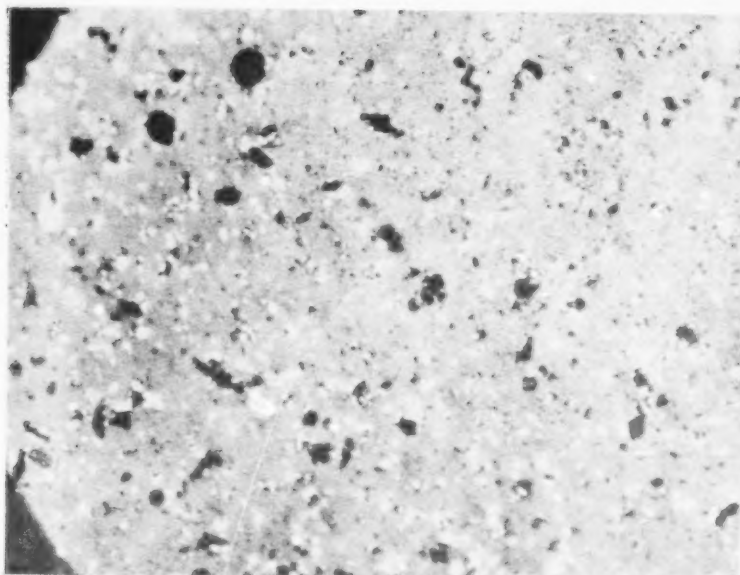


Figure 1. Site M-10; Hi-vol; June 4; (Note large rubber tire fragments); Slightly uncrossed polars (SUP); 163x.

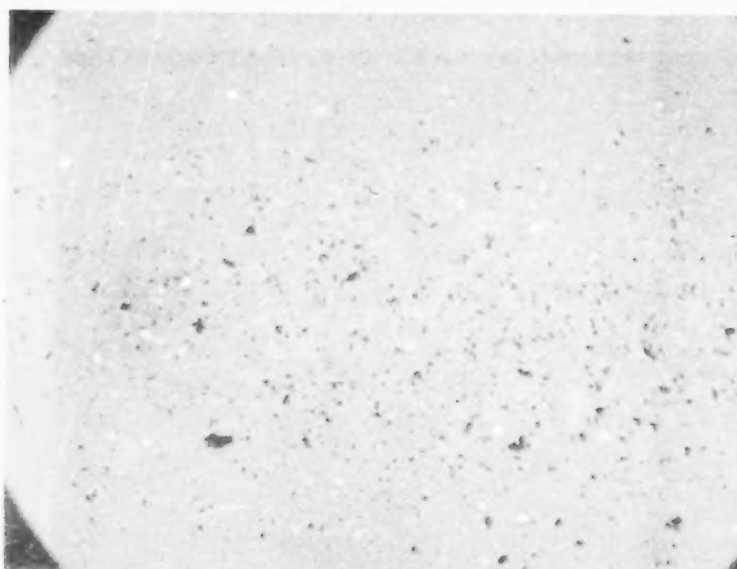


Figure 2. Site M-10; Impactor Stage 3; June 4; SUP; 163x.

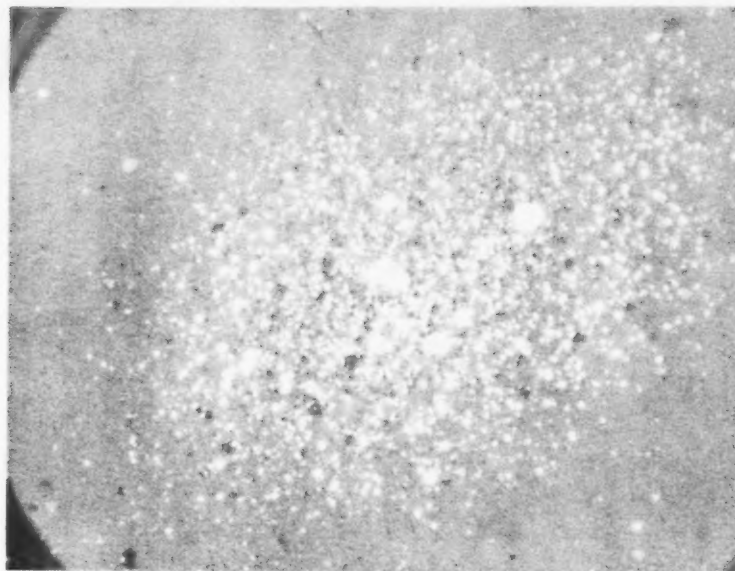


Figure 3. Site M-10; Impactor Stage 4; June 4; SUP; 163x.

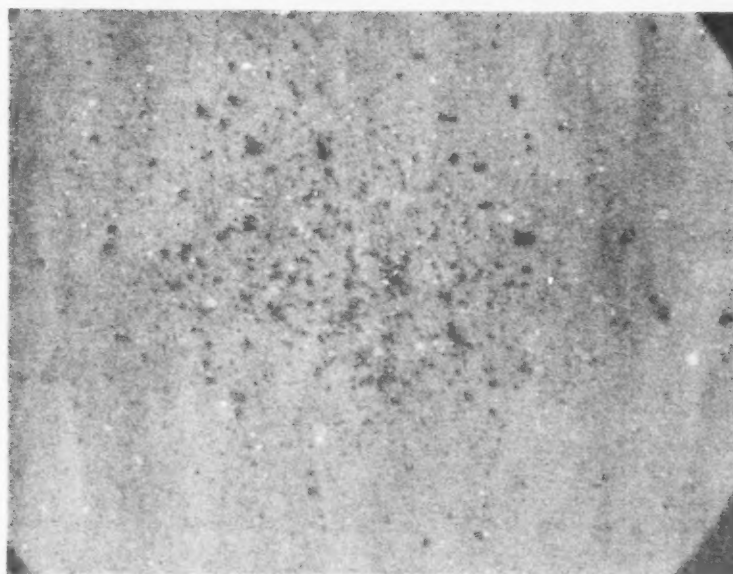


Figure 4. Same sample as Figure 3 after HCl wash. SUP; 163x.

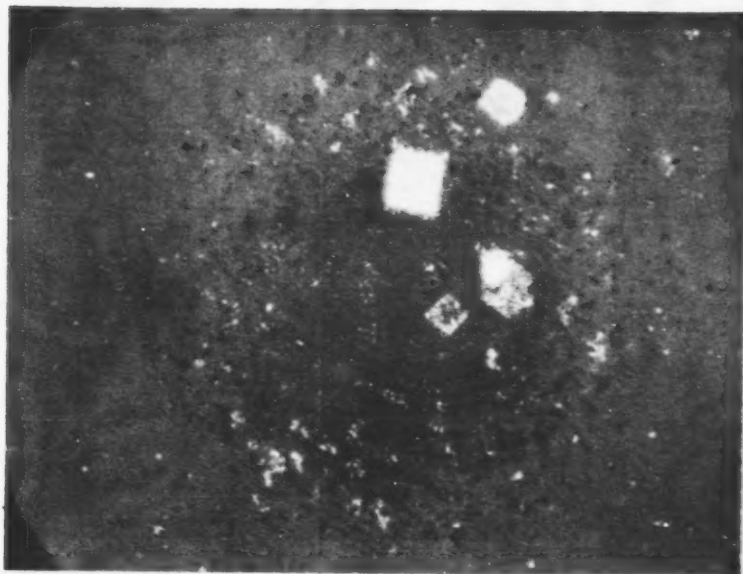


Figure 5. Site M-10; Impactor Stage 7; June 4; SUP; 163x.

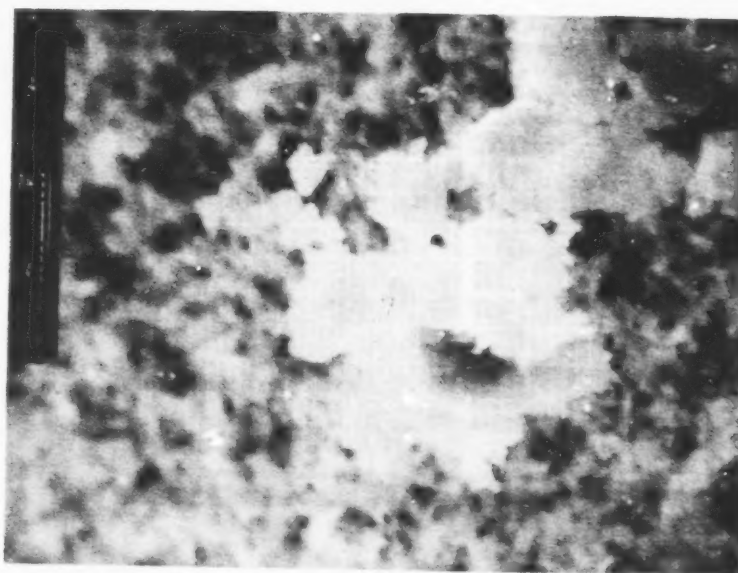


Figure 6. Site M-10; Impactor Stage 0; June 4; (recrystallized calcium carbonate); Secondary electron image (SEI); 3000x.

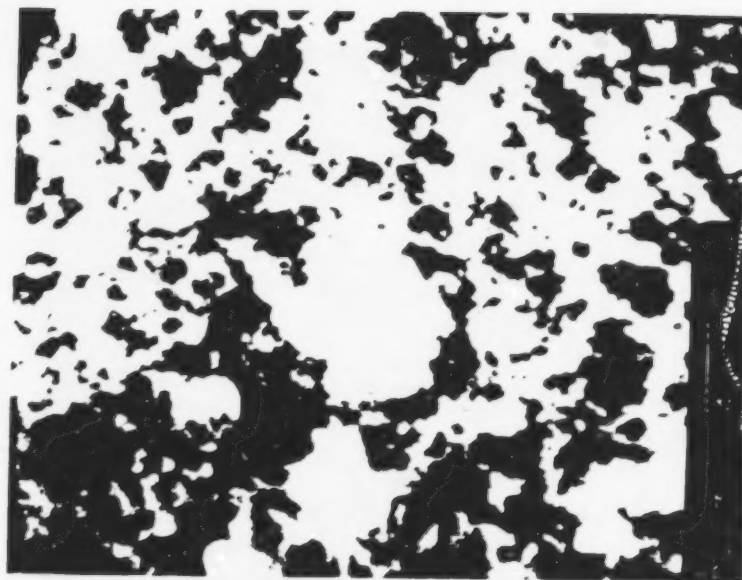


Figure 7. Site M-10; Impactor Stage 3; June 4; SEI; 1000x.

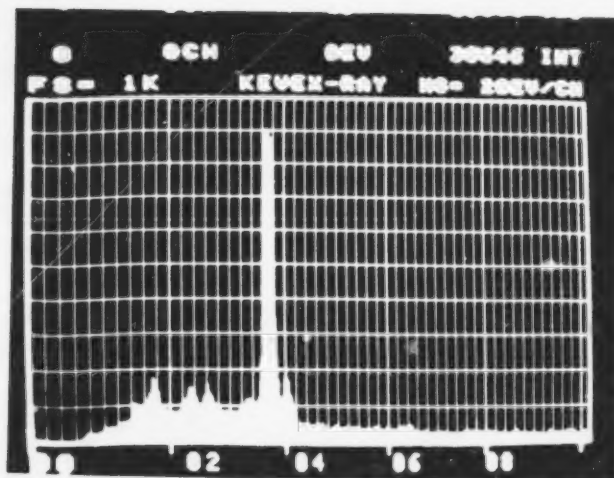


Figure 8. X-ray spectrum of large center particle in Figure 7.

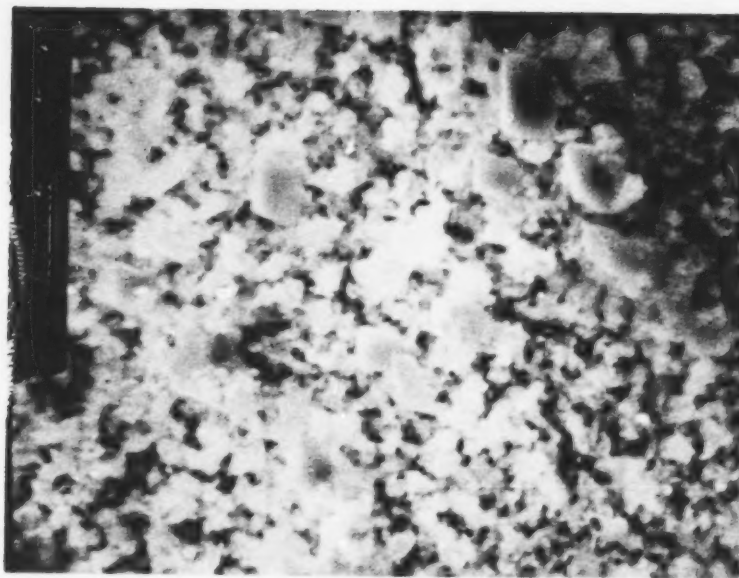


Figure 9. Site M-10; Impactor Stage 5; June 4; SEI; 1000x.

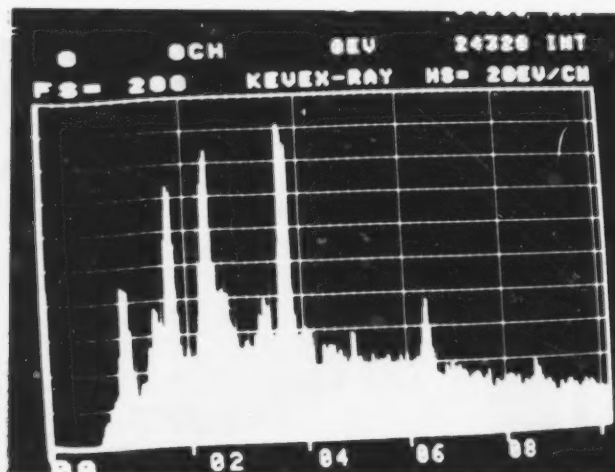


Figure 10. X-ray spectrum of deposition site on Stage 5, Figure 9; Peaks are Mg, Al, Si, S, Cl, K, Ca, and Fe.

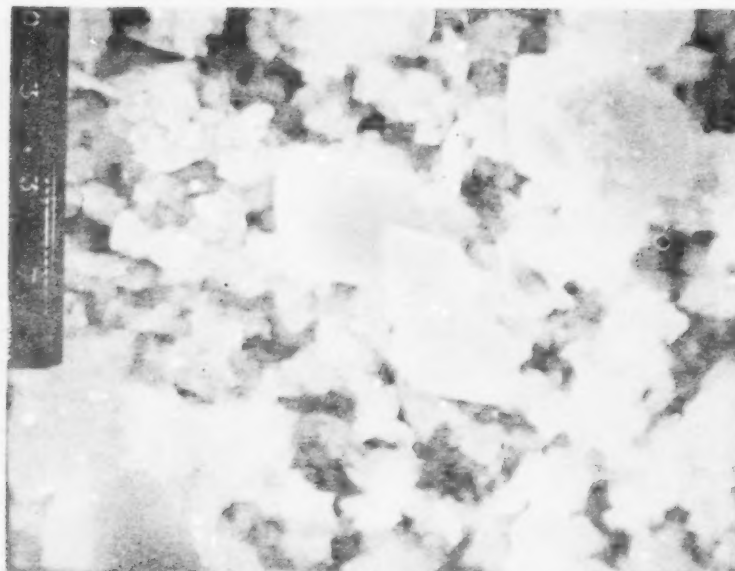


Figure 11. Enlargement of upper cubes in Figure 10; SEI; 3000x.

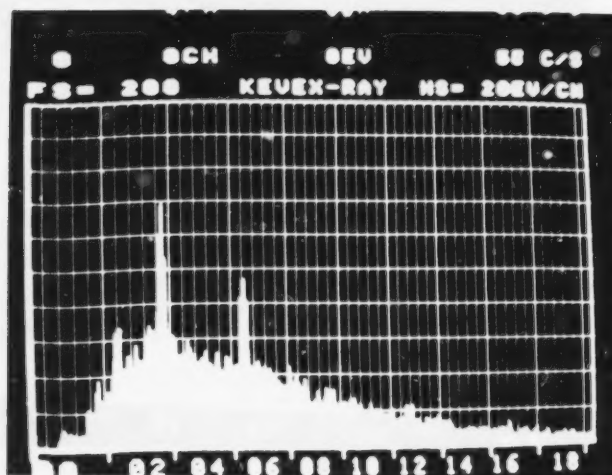


Figure 12. X-ray spectrum of cubes in Figure 11; Three peaks from left to right are S, Ca, and Fe.

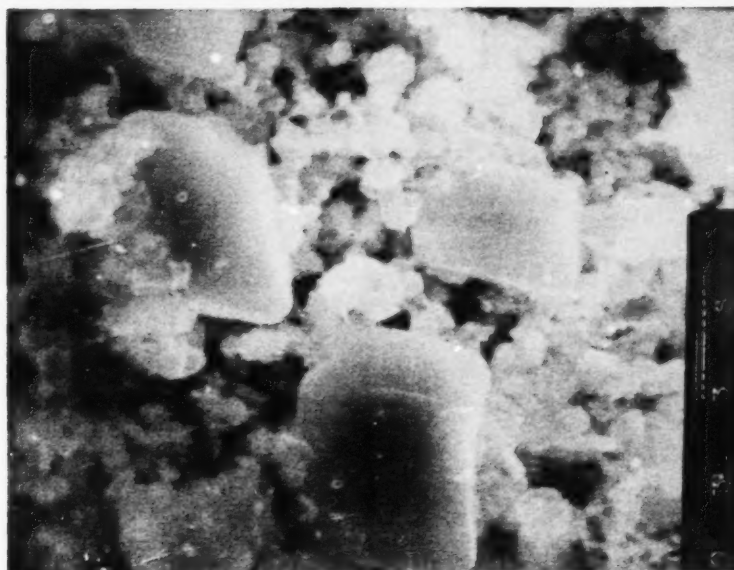


Figure 13. Enlargement of lower left cubes in Figure 9; SEI, 3000x.

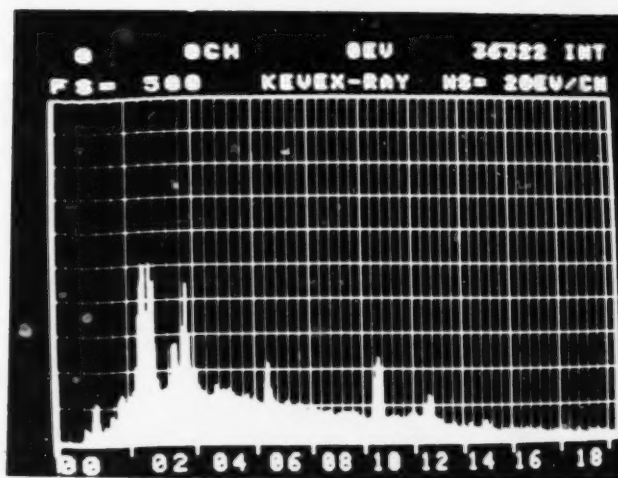


Figure 14. X-ray spectrum of cubes in Figure 13.



Figure 15. Site M-10; Impactor Stage 7; June 4; (Large ammonium sulfate crystals); SEI; 300x.

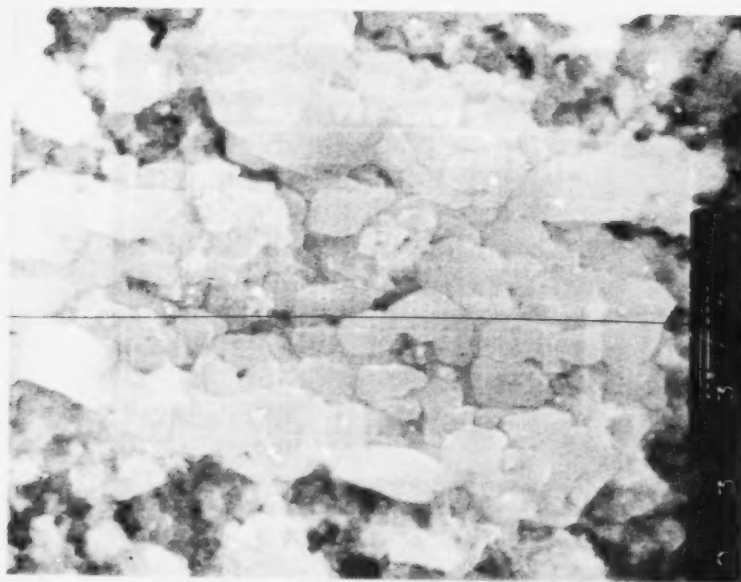


Figure 16. Enlargement of one crystal shown in Figure 15; SEI; 3000x.

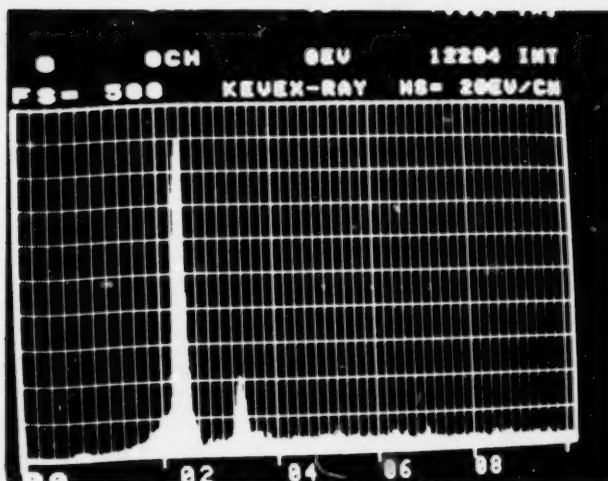


Figure 17. X-ray spectrum of one crystal shown in Figure 15; Large peak is S.

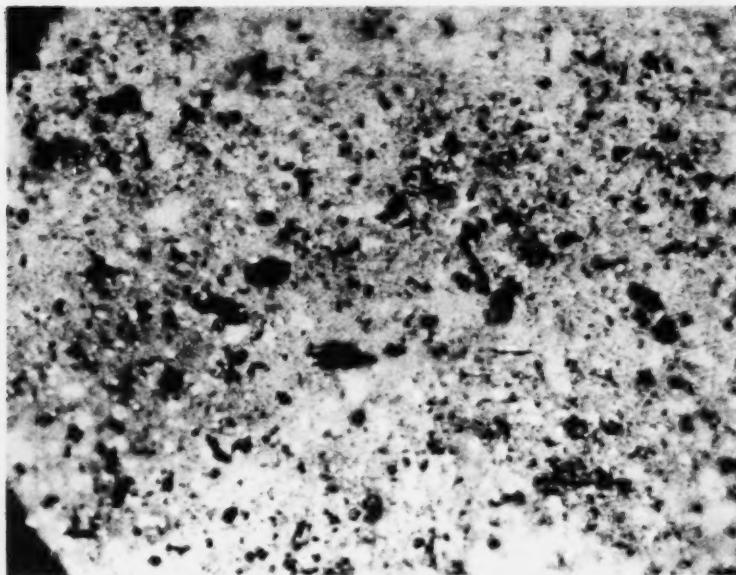


Figure 18. Site M-11; June 4; (Note large rubber tire fragments and fine black carbonaceous particles); SUP; 163x.

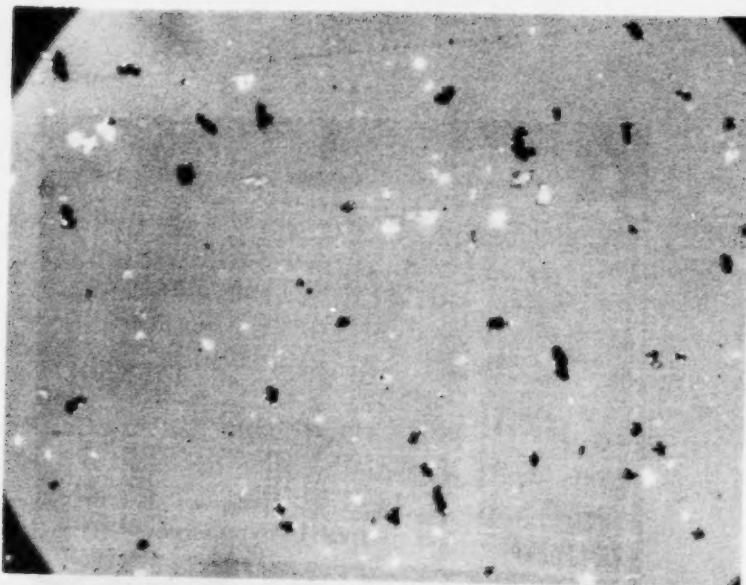


Figure 19. Site M-11; Impactor Stage 0; June 4; (Compare to Figure 28 and note larger amounts of rubber tire dust in Figure 19); SUP; 163x.

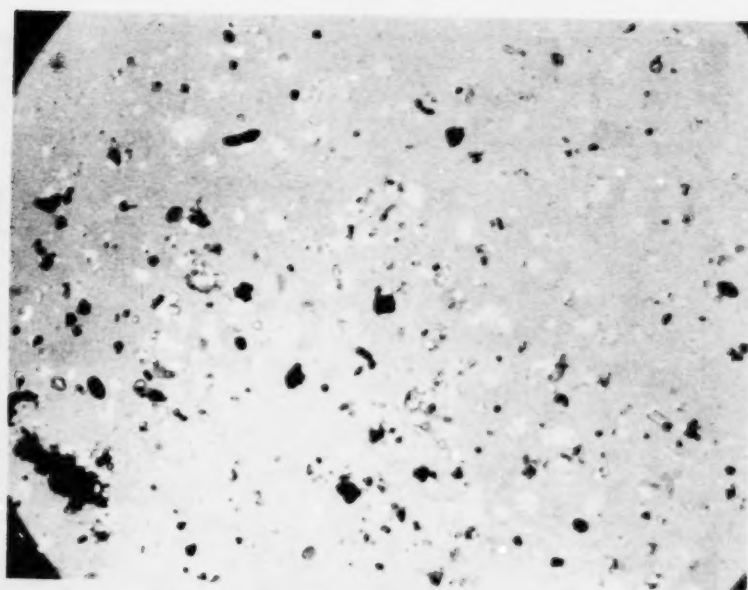


Figure 20. Site M-11; Impactor Stage 3; June 4; SUP; 407x.



Figure 21. Site M-11; Impactor Stage 4; June 4; (Massive white particles are recrystallized calcium carbonate); SUP; 163x.

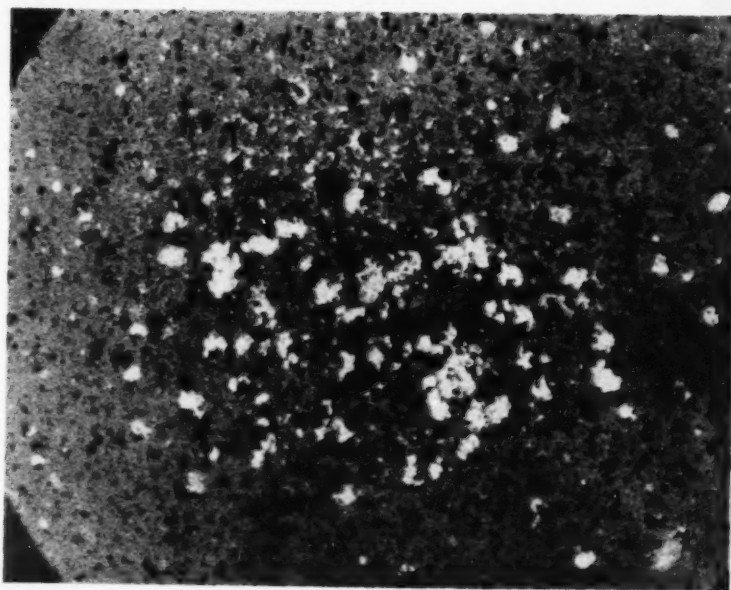


Figure 22. Site M-11; Impactor Stage 5; June 4; SUP; 407x.

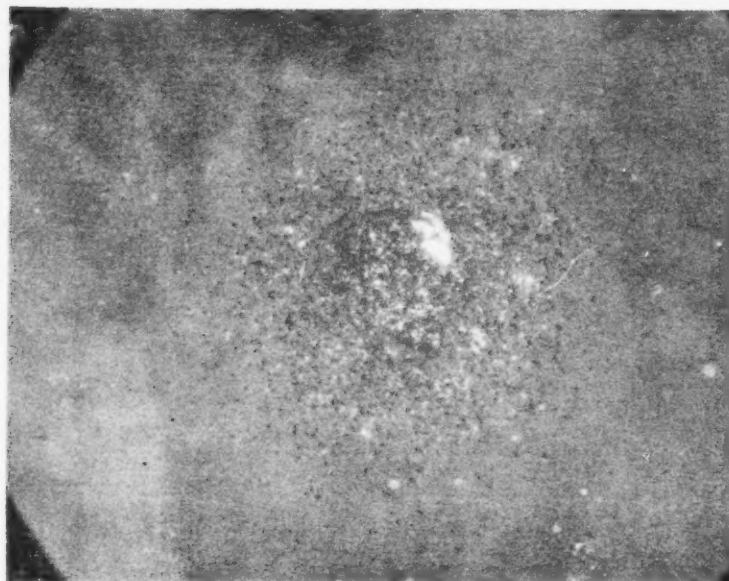


Figure 23. Site M-11; Impactor Stage 6; June 4; (White particles are recrystallized ammonium sulfate); SUP; 163x.

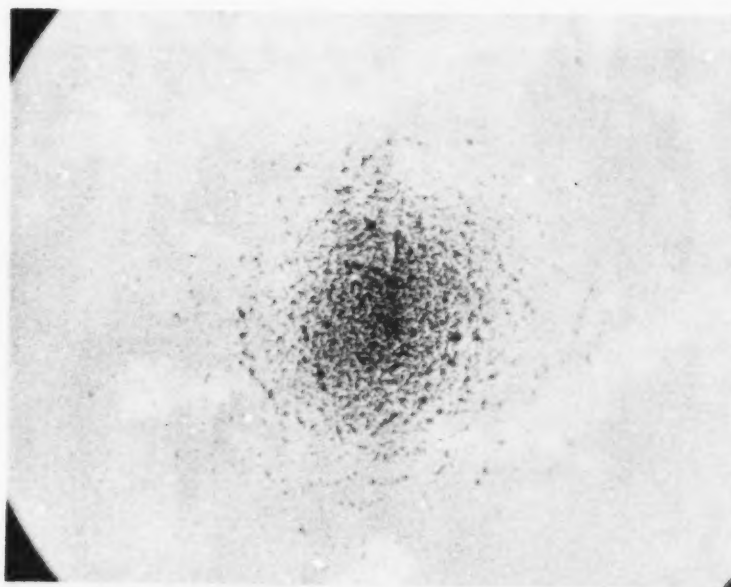


Figure 24. Site M-11; Impactor Stage 7; June 4; Showing submicron auto exhaust particles; Plane polarized light; 163x.

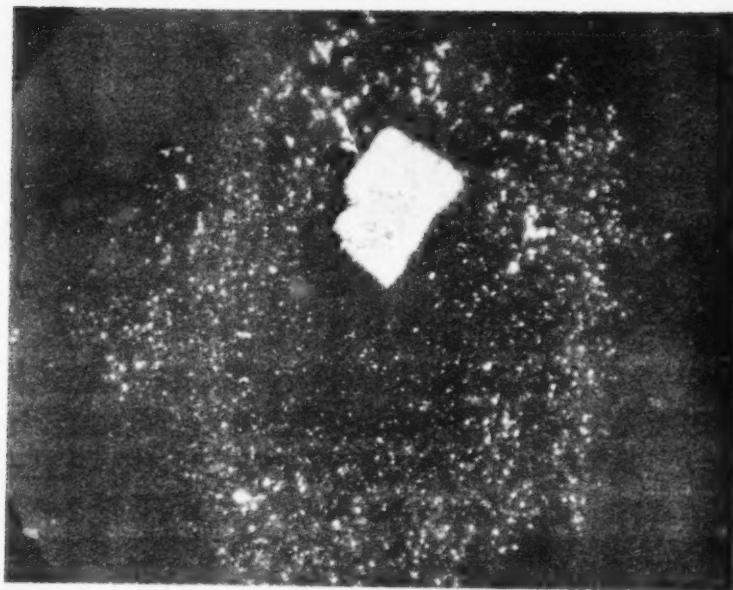


Figure 25. Same sample as Figure 24 with polars crossed to show large ammonium sulfate crystal; 163x.

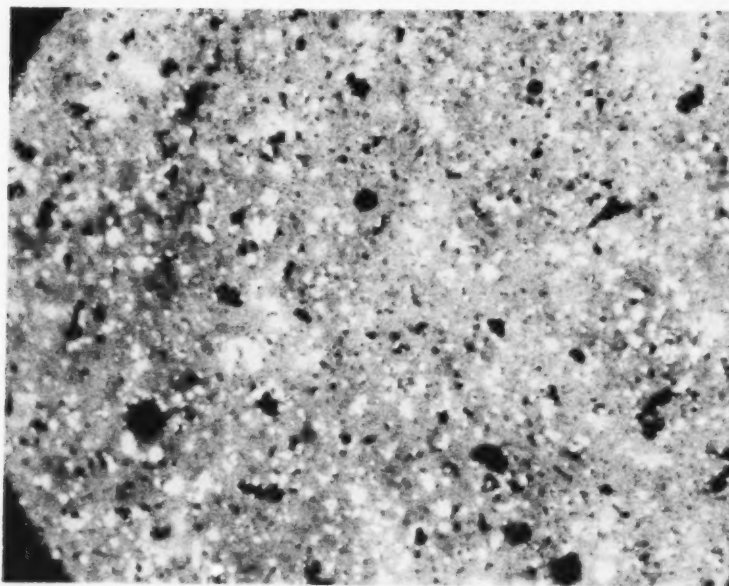


Figure 26. Site M-14; Hi-vol; June 4; SUP; 163x.

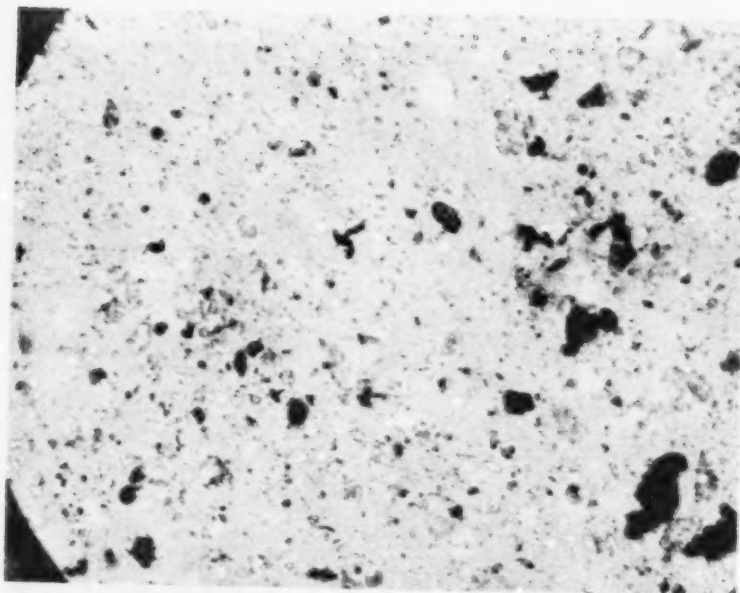


Figure 27. Same sample as Figure 26; SUP; 407x.

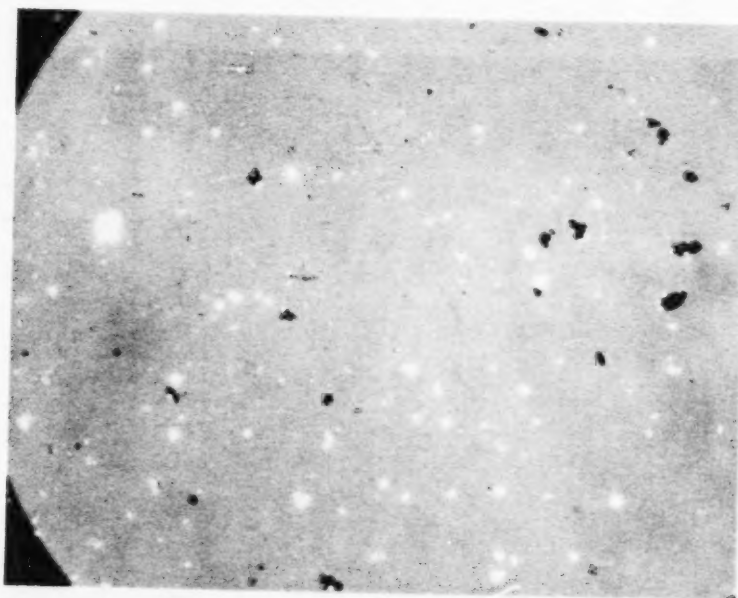


Figure 28. Site M-14; Impactor Stage 0; June 4; SUP; 163x.

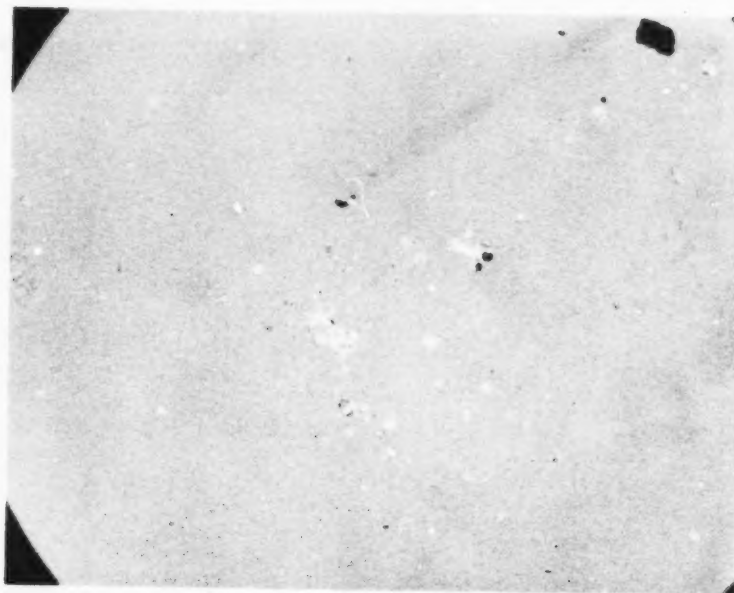


Figure 29. Same sample as Figure 28 showing group of particles recrystallized from liquid; SUP; 407x.

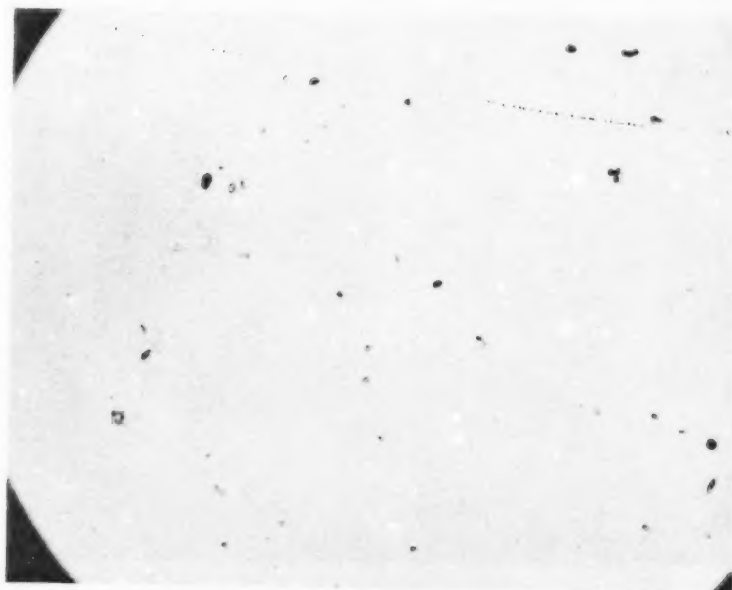


Figure 30. Site M-14; Impactor Stage 1; June 4; SUP; 163x.

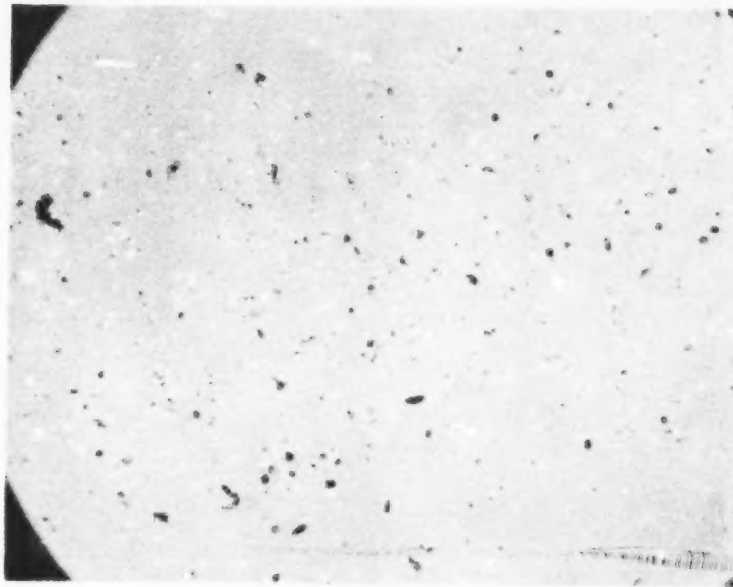


Figure 31. Site M-14; Impactor Stage 2; June 4; SUP; 163x.

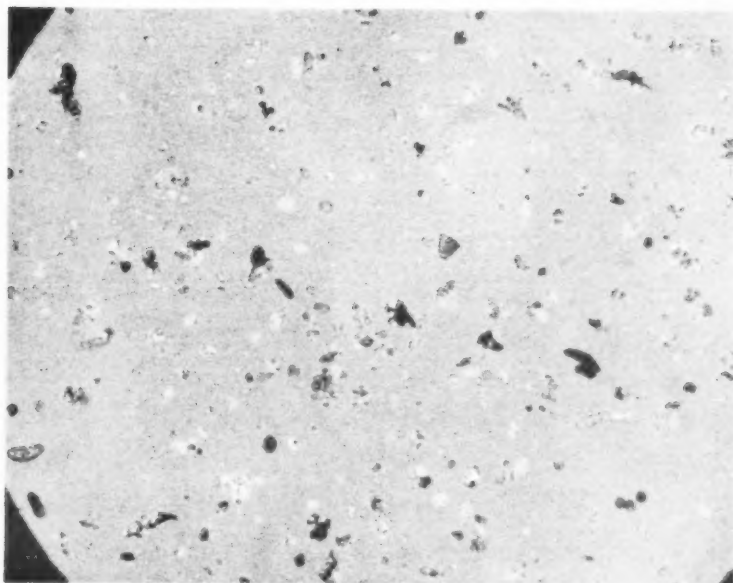


Figure 32. Same sample as Figure 31; SUP: 407x.

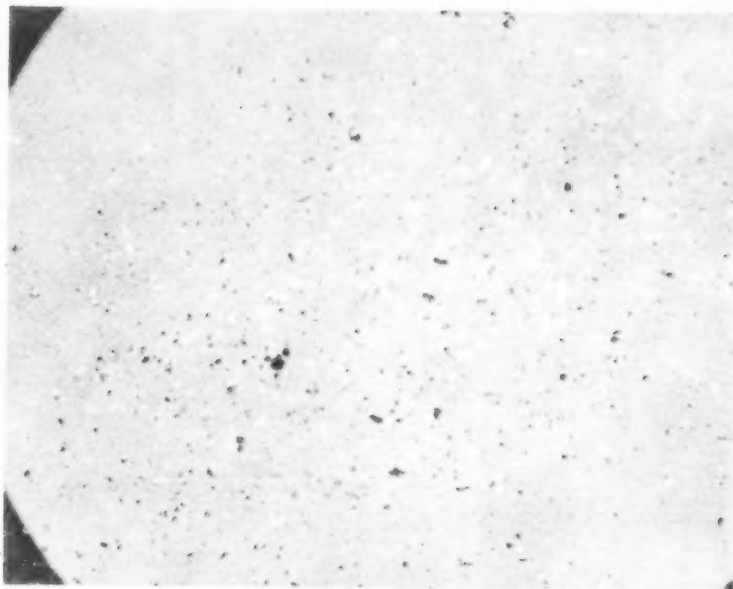


Figure 33. Site M-14; Impactor Stage 3; June 4; (Note large birefringent white particles, which are recrystallized calcium carbonate); SUP; 163x.

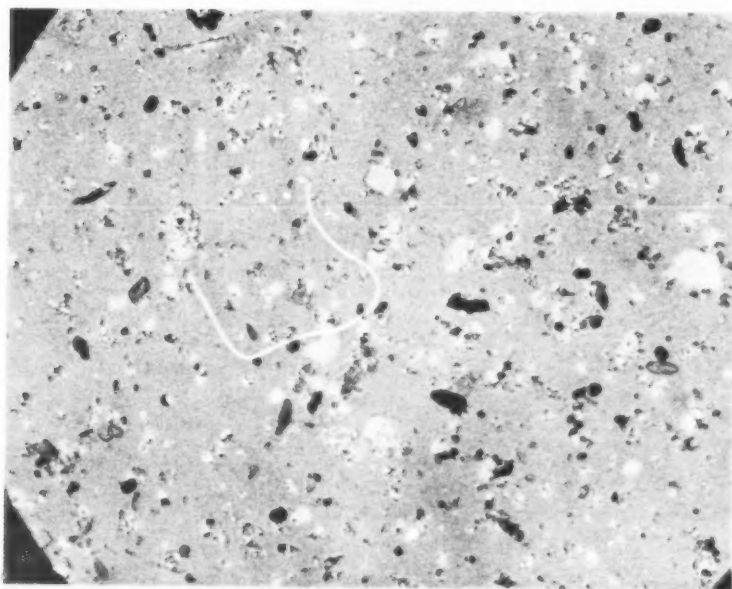


Figure 34. Same sample as Figure 33; SUP; 407x.



Figure 35. Site M-14; Impactor Stage 4; June 4; (Note large masses of recrystallized calcium carbonate); SUP; 163x.



Figure 36. Same sample as Figure 35, rotated 90 to show the structure of recrystallized mass; SUP; 163x.

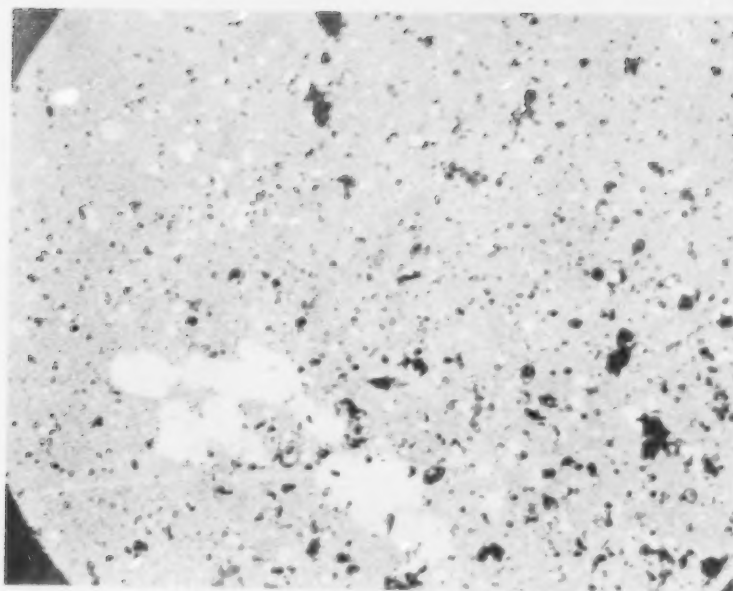


Figure 37. Same sample as Figure 35; SUP; 407x.

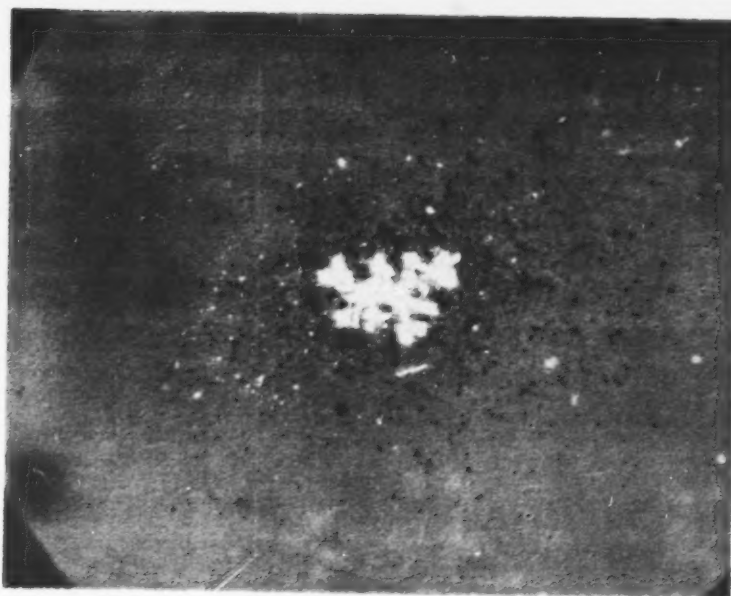


Figure 38. Site M-14; Impactor Stage 5; June 4; (Large white mass is re-crystallized calcium carbonate; small white particles are re-crystallized sulfate); SUP; 163x.

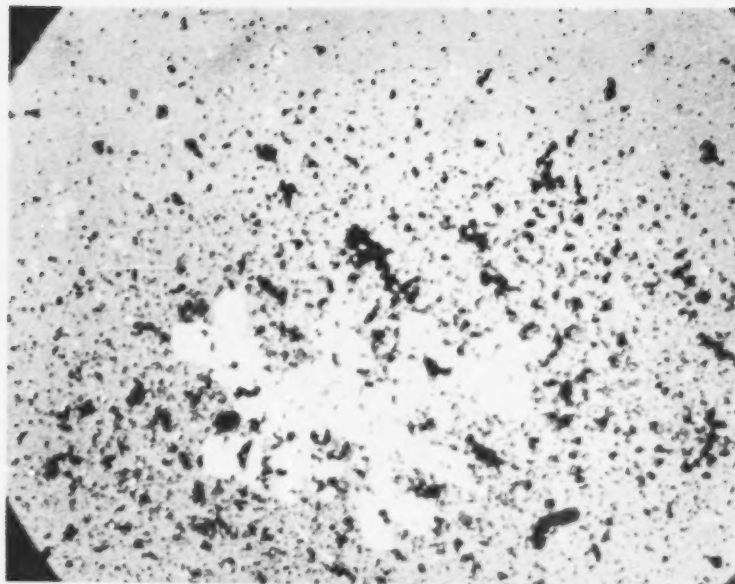


Figure 39. Same sample as Figure 38; SUP; 407x.

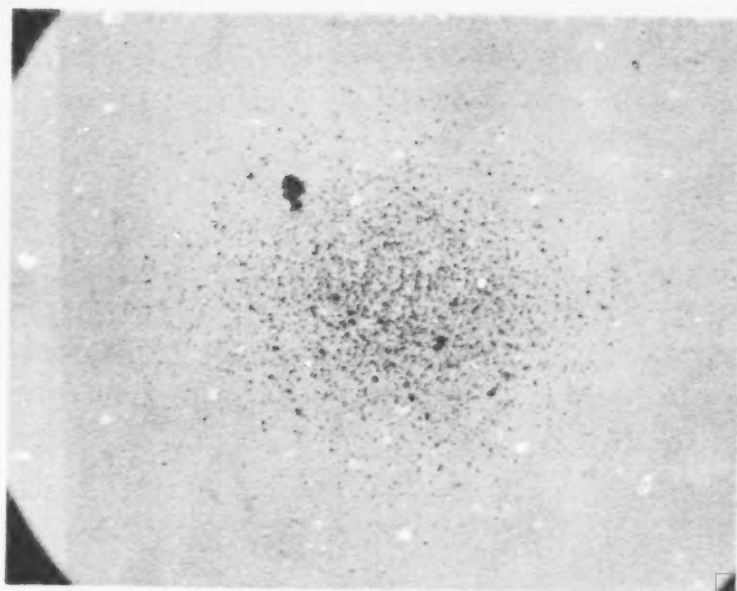


Figure 40. Site M-14; Impactor Stage 6; June 4; SUP; 163x.

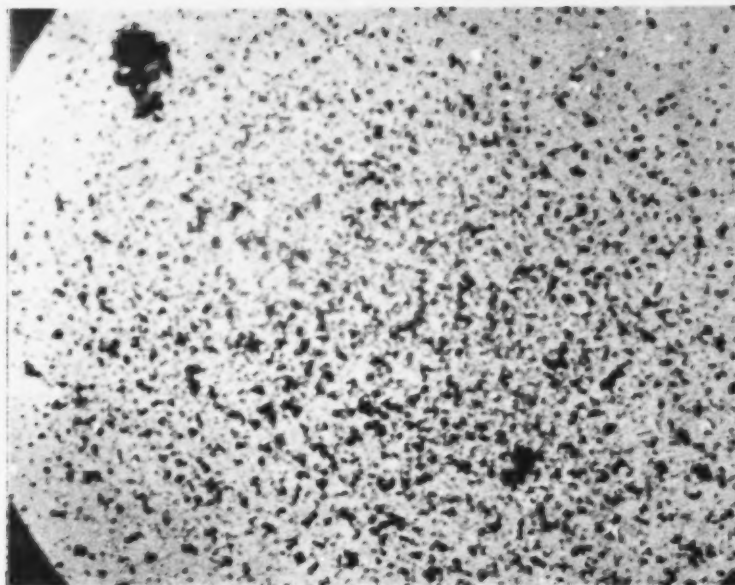


Figure 41. Same sample as Figure 40, showing fine recrystallized sulfate particles; SUP; 407x.

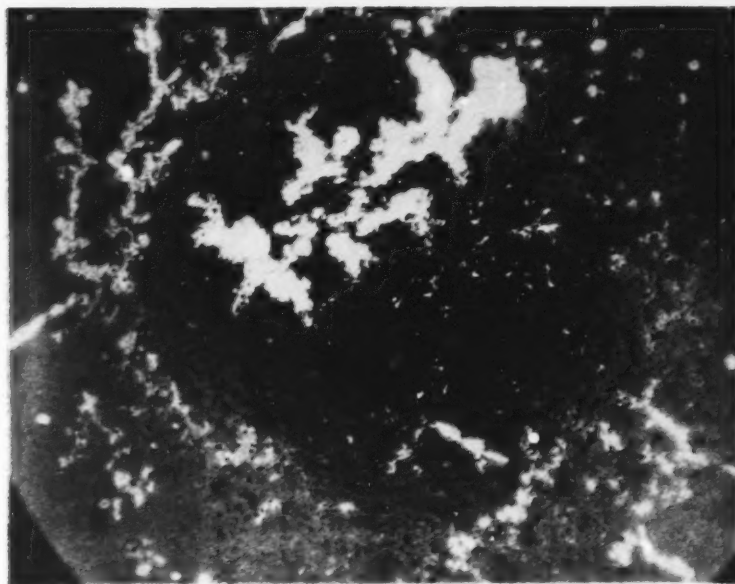


Figure 42. Site M-14; Impactor Stage 7; June 4; (White material is recrystallized ammonium sulfate); SUP; 163x.

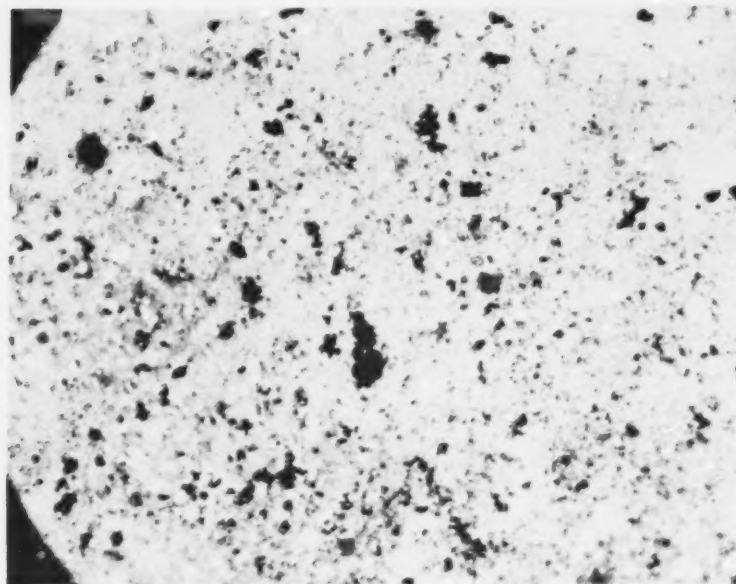


Figure 43. Site M-10; Hi-vol; June 11; SUP; 163x.



Figure 44. Site M-10; Impactor Stage 0; June 11; Nuclepore substrate; SEI; 1000x.



Figure 45. Site M-10; Impactor Stage 4; June 11; Nuclepore substrate; SEI; 1000x.

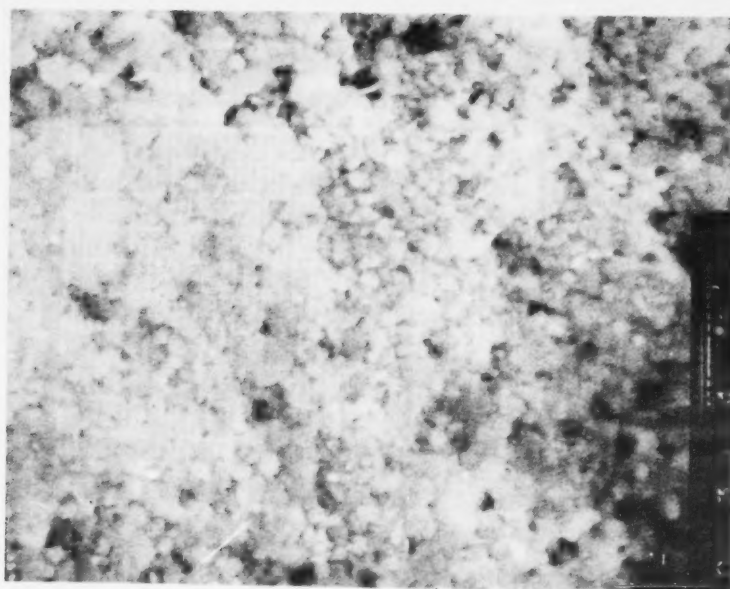


Figure 46. Enlargement of Figure 45; SEI; 1000x.

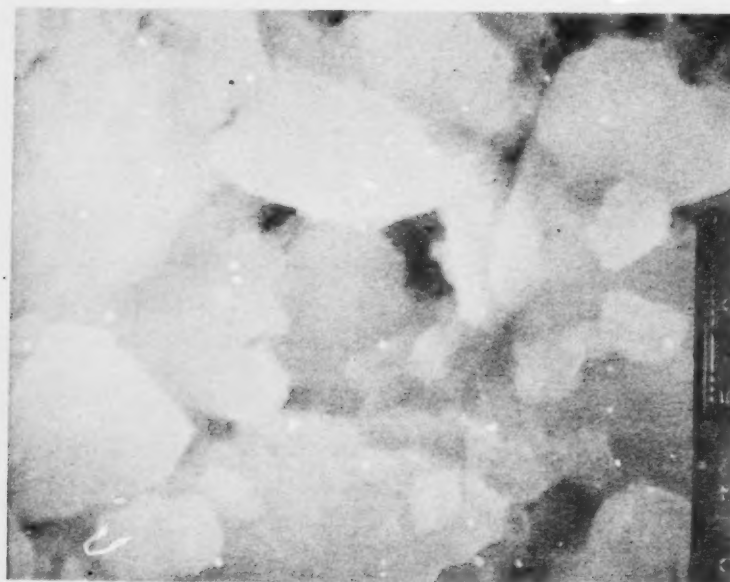


Figure 47. Enlargement of Figure 46; SEI, 10,000x.

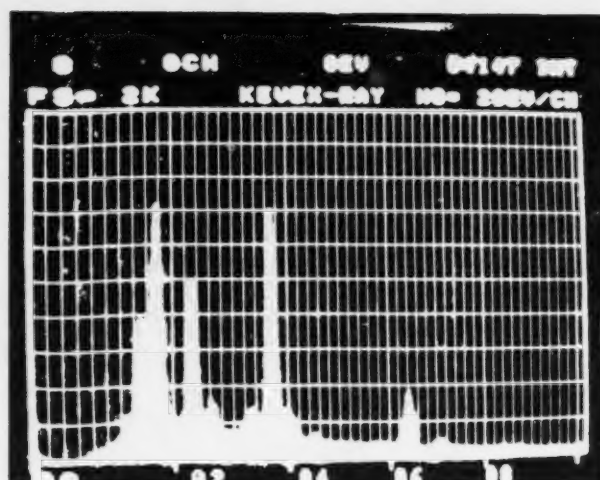


Figure 48. X-ray spectrum of total Stage 4 deposit site (Figure 45); Peaks visible are Mg, Al, Si, S, Cl, K, Ca, Ti, and Fe.

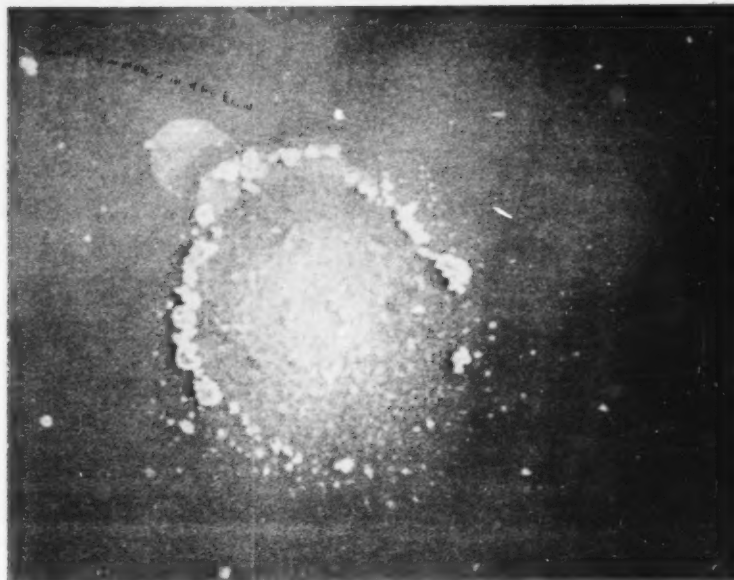


Figure 50. Enlargement of ammonium sulfate ring crystals from Figure 49; SEI; 1000x.

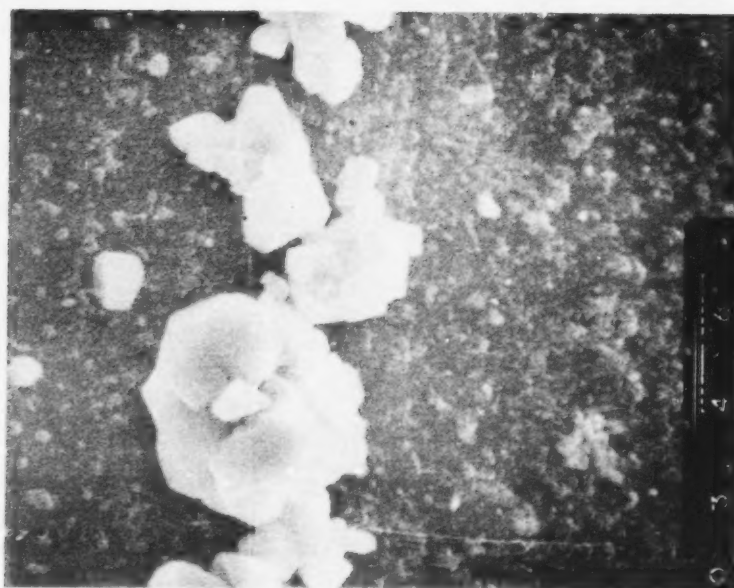


Figure 49. Site M-10; Impactor Stage 7; June 11; Ammonium sulfate crystals surrounding main deposition area; Nuclepore substrate; SEI; 100x.

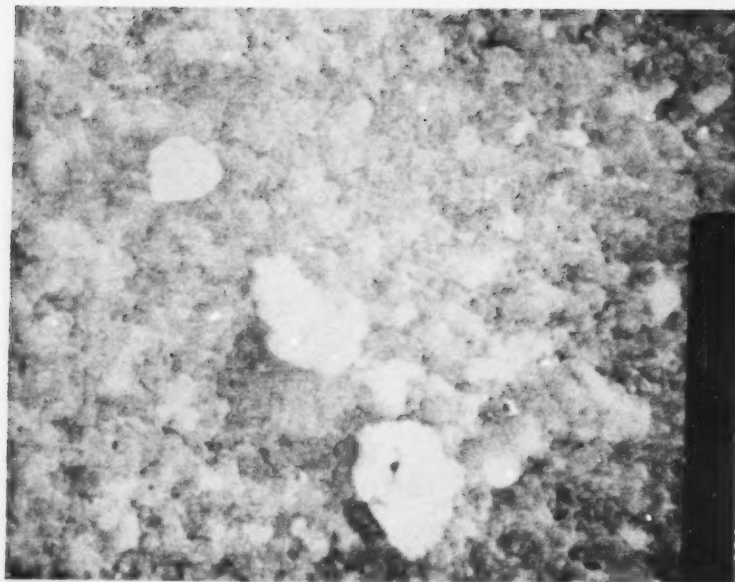


Figure 51. Enlargement of particles in center of deposit in Figure 49; SEI; 10,000x.

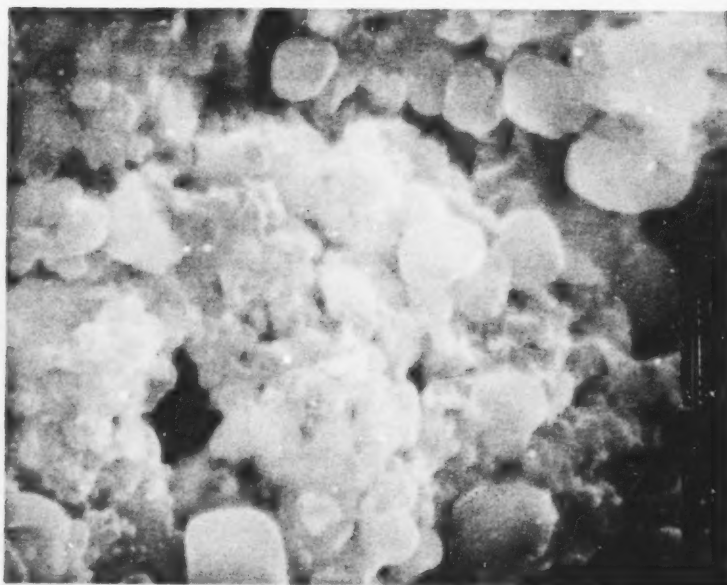


Figure 52. Enlargement of crusted deposit from Figure 49; SEI; 10,000x.

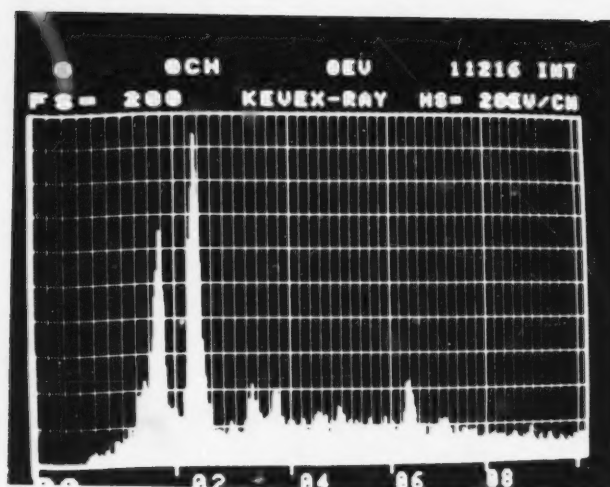


Figure 53. X-ray spectrum of center of deposit (shown in Figures 49 and 52); Peaks for Al, Si, S, K, Ca, and Fe are present.

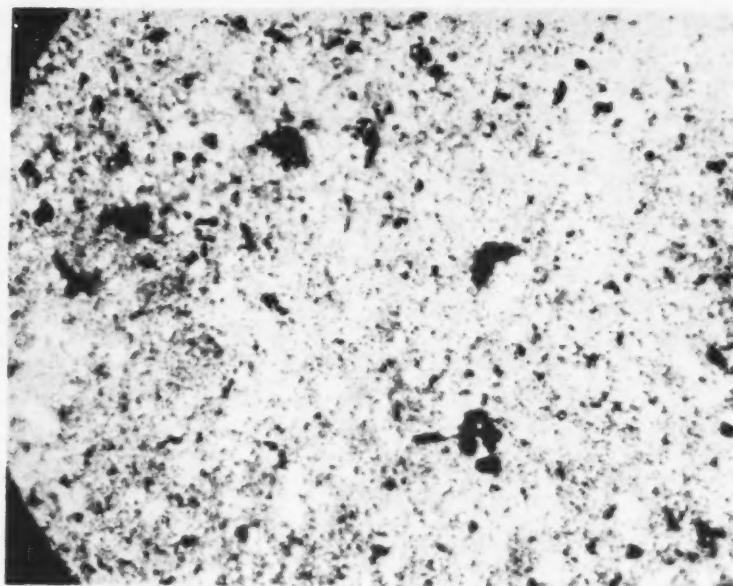


Figure 54. Site M-11; Hi-vol; June 11; SUP; 163x.

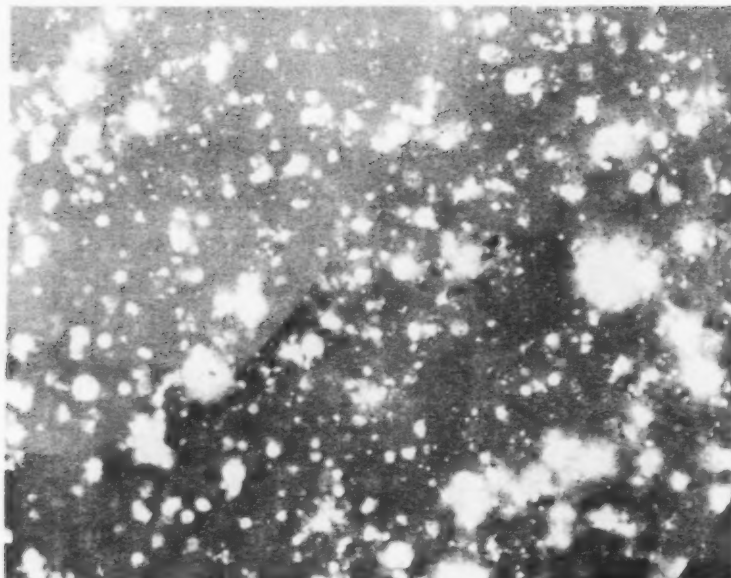


Figure 55. Same sample as Figure 54 with polars completely crossed to show birefringent spherical particles; 407x.



Figure 56. Site M-11; Impactor Stage 3; June 11; Nuclepore substrate; SEI; 300x.

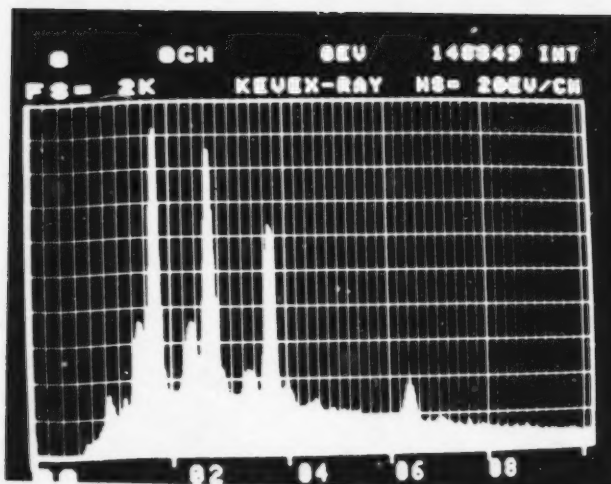


Figure 57. X-ray spectrum of whole deposit pictured in Figure 56; Elemental peaks are for Na, Mg, Al, Si, S, Cl, K, Ca, Ti, and Fe.

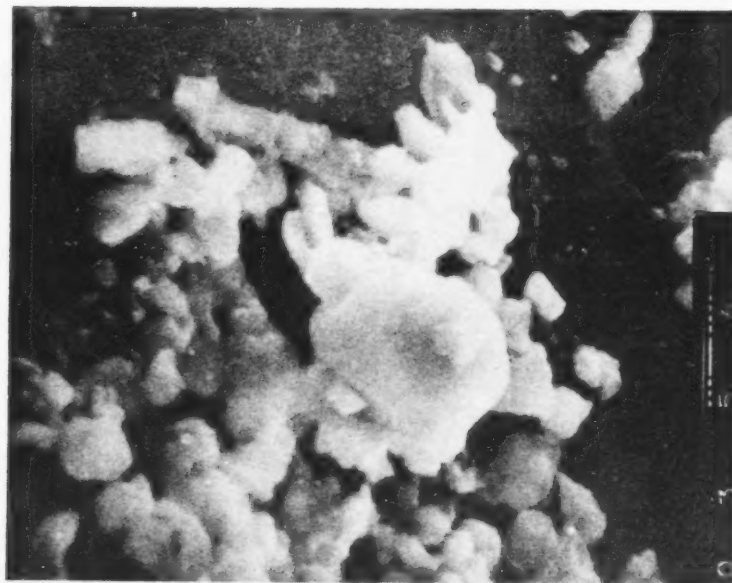


Figure 58. Enlargement of Figure 56; (Large crystal is primarily NaCl with traces of S, Mg, Cl, and Ca, and therefore is sea salt); SEI; 3000 3000x.

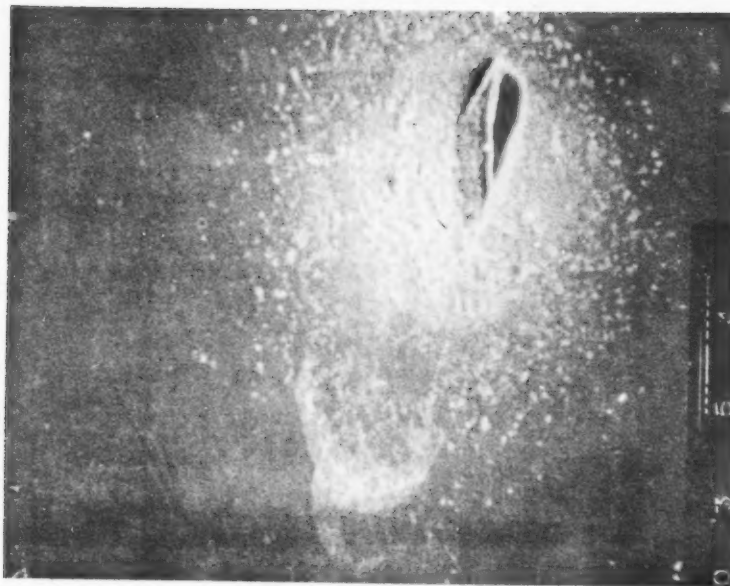


Figure 59. Site M-11; Impactor Stage 7; June 11; Nuclepore substrate; Large upper right crystal is ammonium sulfate; SEI; 300x.

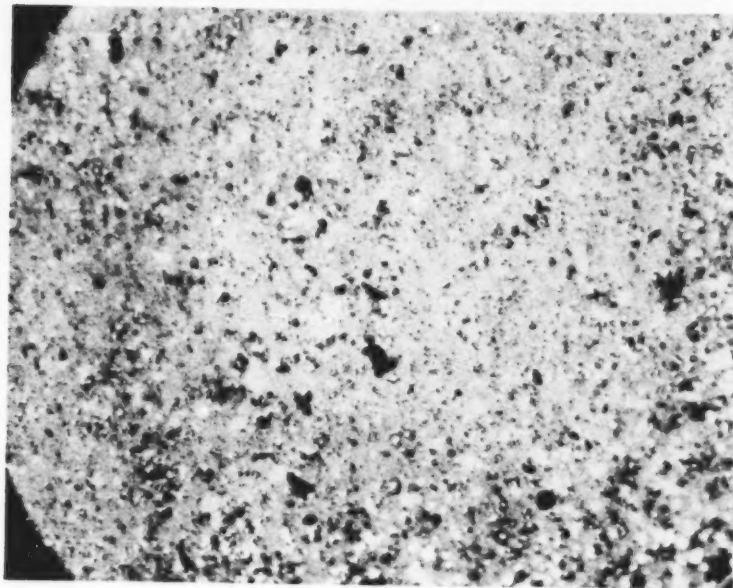


Figure 60. Site M-14; Hi-vol; June 11; SUP; 163x.

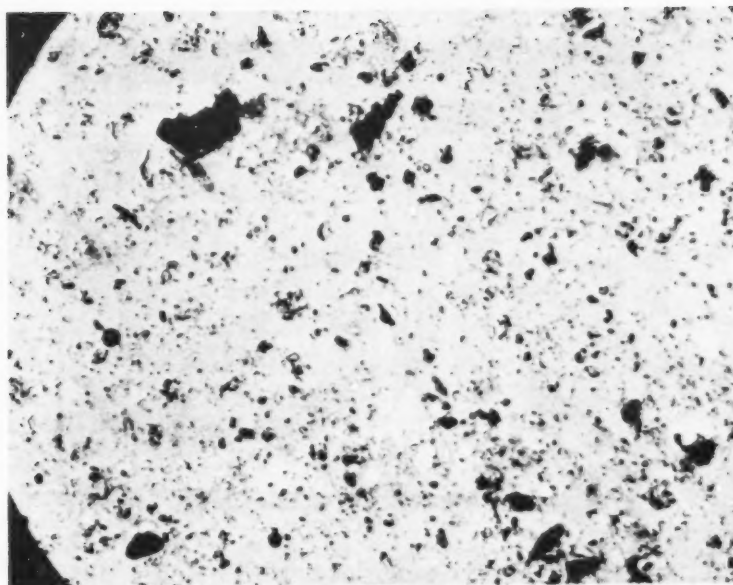


Figure 61. Same sample as Figure 60; SUP; 407x.



Figure 62. Site M-14; Impactor Stage 0; June 11; Nuclepore substrate; Cubical particle is NaCl; Amorphous particle is calcium (carbonate); SEI; 3000x.

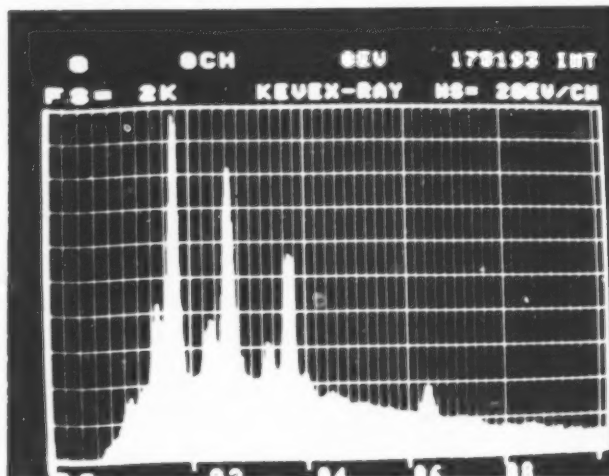


Figure 63. Site M-14; Impactor Stage 3; June 11; X-ray spectrum of whole sample; Peaks present are Na, Mg, Al, Si, S, Cl, K, Ca, Ti, and Fe.



Figure 64. Site M-14; Impactor Stage 3; June 11; Nucleopore substrate; SEI; 3000x.

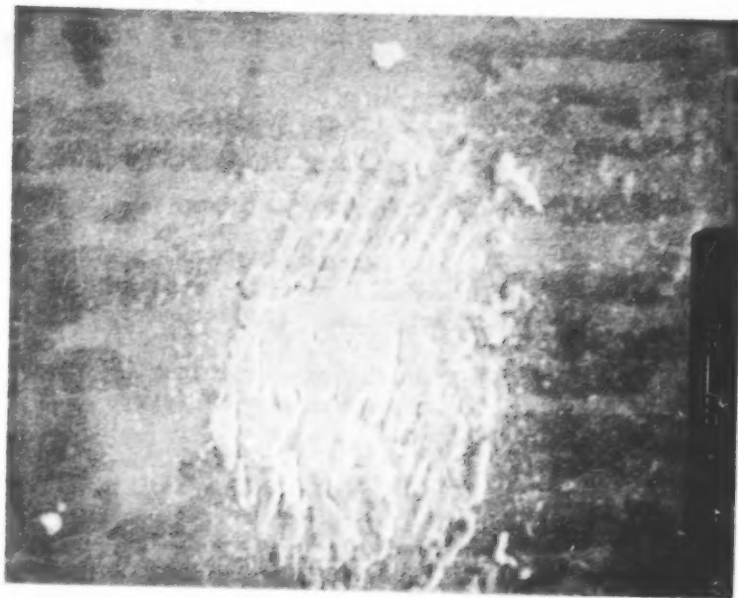


Figure 65. Site M-14; Impactor Stage 7; June 11; Nuclepore substrate; SEI; 300x.

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